

5.3700(B)

5(3)

67947

SO: 20-130-1-20/69

AUTHORS: Andrianov, K. A., Corresponding Member AS USSR, Zhdanov, A. A.,
Odinets, V. A.

TITLE: Chloromethylation of Aryl-aliphatic Disiloxanes. Synthesis of
Chloromethylbenzyltrimethylchlorosilane and Its Derivatives

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 1, pp 75-78 (USSR)

ABSTRACT: The authors proved that the chloromethylation of the benzyl group bound to silicon can be successfully used for the synthesis mentioned in the subtitle (see Scheme). This reaction proceeds well in fuming hydrochloric acid. Paraform is used as an agent of chloromethylation. The chloromethylation in the presence of zinc chloride is accompanied by secondary processes. They form viscous, nondistillable products containing diphenyl-methane groups (see Scheme). The isolation of pure chloromethylbenzyltrimethylchlorosilane from the reaction mixture was attained by hydrolysis with excess water while the disiloxane mixture was split by strong sulfuric acid in the presence of ammonium chloride (see Scheme). The total yield in chloromethylbenzyltrimethylchlorosilane was 60% of the benzyltrimethylchlorosilane reacted, and 30% of the quantity used respectively. Direct fractionation of the chloromethylation products purified with water in the vacuum delivered smaller

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~~5(3)~~

AUTHORS:

Golubtsov, S. A.,

Andrianov, K. A., Corresponding Member, AS USSR,

Tishina, N. N.

⁶⁸⁸¹²
S/020/60/131/01/025/060
B011/B006

TITLE:

Reaction of Joint Phenylation of Trichlorosilane and Silicon Tetrachloride

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 1, pp 91-93 (USSR)

ABSTRACT:

The authors intended to eliminate the side reactions which lower the yield to 40% theoretical phenyltrichlorosilane (Ref 5), and at the same time tried to phenylate the silicon tetrachloride formed in the reaction. They found that the hydrogenation of silicon tetrachloride with hydrogen proceeds satisfactorily, if the reagents are heated under the same conditions as bring about the phenylation of trichlorosilane (440-460°, 180 atm). The results obtained proved that it is fundamentally possible to phenylate SiCl_4 , if it is first hydrogenated to trichlorosilane, and only then reacted with benzene. The hitherto unused hydrogen formed as a by-product

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Reaction of Joint Phenylation of Trichlorosilane
and Silicon Tetrachloride

S/020/60/131/01/025/060
B011/B006

in reaction (1) was utilized for the first stage of this process. For this purpose, the authors reacted a mixture of SiCl_4 , C_6H_6 , and trichlorosilane (Ref 6) under the above-mentioned reaction conditions. The molar ratio of trichlorosilane : SiCl_4 was varied between 0.25 : 0.75 and 0.85 : 0.15.

It can be seen from figure 1 that the yield in phenyltrichlorosilane (in g-mol per 100 g-mol of reacted trichlorosilane) increases with increasing content of SiCl_4 in the reaction

mixture. This cannot be explained by the suppression of the disproportionation of trichlorosilane, occurring as a side reaction, since the yield in phenyltrichlorosilane often considerably exceeds 100 g-mol per 100 g-mol trichlorosilane. This proves that the phenylation proceeds according to the intended scheme (see scheme given), under utilization of the hydrogen formed in reaction (1). The increased hydrogen pressure facilitates the first reaction, i.e. hydrogenation. For this reason phenyltrichlorosilane, final product, was obtained in much higher yield than is obtainable at at-

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and Silicon Tetrachloride

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B011/B006

mospheric pressure. The authors have thus proved that the phenylation of SiCl_4 with benzene gives sufficiently high yields even without use of metalorganic compounds, if conditions are so chosen, that SiCl_4 is hydrogenated by hydrogen to the intermediate trichlorosilane according to reaction (2). Trichlorosilane then reacts with benzene and forms phenyl-trichlorosilane, regenerating hydrogen. There are 1 figure and 6 references, 5 of which are Soviet. ✓

SUBMITTED: November 5, 1959

Card 3/3

5.37008

AUTHORS:

Andrianov, K. A., Corresponding
Member, AS USSR, Kurasheva, N. A.

69506

S/020/60/131/04/029/073
B011/B017

TITLE:

On the Reaction of Titanium Tetrachloride With Hexamethyldisiloxane¹

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 4, pp 825-826 (USSR)

TEXT: The experiments carried out by the authors have shown that the effect produced by titanium tetrachloride above 100° causes a rupture of the siloxane bond in hexamethyldisiloxane. In this connection, trimethylsiloxychloro derivatives of titanium are formed. If this reaction takes place at 120-200°, only trimethylchlorosilane and trimethylsiloxyltrichlorotitanium¹ (yield 69.8%) are formed (see Scheme). All efforts to obtain products of higher degrees of substitution (i.e. bis-(trimethylsiloxy)-dichlorotitanium) failed. The latter compound, however, was formed in a yield of 34.7% at 280-350° due to another reaction scheme (see this one). This indicates that the halogen on the titanium atom is replaced by the second siloxy group, probably due to the reaction of trimethylsiloxytrichlorotitanium with hexamethyldisiloxane. Experiments carried out with these two substances at 280-320° yielded bis-(trimethylsiloxy)-dichlorotitanium in a yield of 43.0% (see Scheme). The mechanism of rupture of siloxane bonds during the reaction mentioned in the title proceeds, according to the authors, in the following manner: the titanium atom in $TiCl_4$ is coordinated with the oxygen of hexamethyldisiloxane

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69506

On the Reaction of Titanium Tetrachloride With
Hexamethyldisiloxane

S/020/60/131/04/029/073
B011/B017

under formation of a transition complex (I). The further process is accompanied by the rupture of the siloxane bond due to the redistribution of the electron density. Titanium is added to oxygen, and trimethylchlorosilane and trimethylsiloxytrichlorotitanium (II) are formed. The addition of the second siloxy group to the titanium atom probably takes place through the coordination of the titanium atom of trimethylsiloxytrichlorotitanium with hexamethyldisiloxane (III). In the following, trimethylchlorosilane and bis-(trimethylsiloxy)-dichlorotitanium (IV) are formed. There are 6 references, 2 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of
Sciences, USSR)

Card ~~2/3~~

84671

S/020/60/134/006/014/031
B016/B067

158114

AUTHORS: Andrianov, K. A., Corresponding Member AS USSR and
Severnnyy, V. V.

TITLE: Telomerization ¹ Reaction of Organo-cyclosiloxanes ¹

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 134, No. 6,
pp. 1347-1349

TEXT: The use of telomerization reaction in organosilicon compounds is rendered difficult due to the lack of elemental-organic monomers with double bonds between element and oxygen, and capable of polymerization. The authors, however, effected the telomerization of octamethyl cyclo-tetrasiloxane as cyclic compound and dimethyl dichlorosilane as a substance effecting the rupture of the molecular chain. Experiments showed that, in addition, the former compound is polymerized by the latter. The authors found that the reaction of the ring cleavage without catalysts proceeds rapidly at 200-250°C. At a ratio between the first and the second substance of 2 : 1 it was completed at 250°C within 3 hours. Oligomers were obtained corresponding to the compounds of the

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84671

Telomerization Reaction of Organo-
cyclosiloxanes

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following reactions: $n(M_2SiO)_4 + M_2SiCl_2 \rightarrow Cl-(M_2SiO-)_{4n}-M_2SiCl_2$; ($M=CH_3$).

These results were reproduced by repeated experiments. In their experiments the authors obtained about 75% of reaction products which can be distilled below 260°C at 3 torr; only 25% boiled at higher temperatures. The following compounds were isolated by rectifications: α,ω -dichloro decamethyl pentasiloxane ($n = 1$), yield 16.7%, α,ω -dichloro-octadecamethyl nonasiloxane ($n = 2$), yield 20.0%, and α,ω -dichloro hexacosamethyl tridecasiloxane ($n = 3$), yield 7.7%. Table 1 gives the physical properties of these products. The formation of oligomers with 5, 9, and 13 silicon atoms in the molecule indicates a successive addition of the molecules of octamethyl cyclotetrasiloxane to dimethyl dichlorosilane. Apparently the reaction is initiated by the coordination of one of the oxygen atoms of octamethyl cyclotetrasiloxane with the silicon atom of dimethyl dichlorosilane. Due to the weakening of the Si-O bond in the former the strained ring is ruptured with chlorine being added to the silicon atom, whereas dimethyl dichlorosilane is added to the oxygen. The further growth of the chain is probably due to the coordination of the silicon final atoms and the oxygen of the cyclic product. This is

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Telomerization Reaction of Organo-
cyclosiloxanes

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B016/B067

followed by the rupture of the ring and the formation of a linear α,ω -dichloro dimethyl siloxane. These presumable reaction mechanisms are explained by schemes. The authors continue the study of this reaction by the example of similar cycles, and they investigated further reagents effecting the rupture of the molecular chain. There are 3 tables and 11 references: 4 Soviet, 4 US, 1 British, and 1 Japanese.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds of the
Academy of Sciences. USSR)

SUBMITTED: July 9, 1960

X

Card 3/3

86393

S/020/60/135/002/018/036
B016/B052

15.8116

AUTHORS: Andrianov, K. A., Corresponding Member of the AS USSR,
and Kurasheva, N. A.

TITLE: The Reaction of Heterofunctional Condensation of
Bis-(trimethylsiloxy) Titanium Dichloride With
Phenyl-methyl Diethoxysilane

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 2,
pp. 316 - 319

TEXT: The authors studied the reaction of heterofunctional condensation between bis-(trimethylsiloxy) titanium dichloride and phenyl-methyl diethoxysilane at 150°C. They found that not ethyl chloride, but trimethyl silane chloride is split off under the formation of a polymer. The chemical composition of this polymer is given by equation I of the attached scheme. The polymer is easily soluble in benzene and toluene, highly elastic at room temperature, and becomes brittle (in thin filaments) under humid conditions. This reaction which differs from that of alkyl-(aryl)-halide silanes with alkyl-(aryl)-ethoxy silanes, was

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The Reaction of Heterofunctional Condensation
of Bis-(trimethylsiloxy) Titanium Dichloride
With Phenyl-methyl Diethoxysilane

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thoroughly studied. It is shown that not only phenyl-methyl diethoxy-silane but also dimethyl butoxysilane reacts with bis-(trimethylsiloxy) titanium dichloride to form trimethyl silane chloride instead of butyl chloride. The chemical composition of the resulting polymer indicates that the reaction described here is very complicated. Further experiments proved that the reaction is initiated by humid air reacting with bis-(trimethylsiloxy) titanium dichloride. Thus, HCl is split off (Scheme II (1)). The initial reaction product reacts with phenyl-methyl diethoxysilane while alcohol is separated. HCl reacts with the trimethyl siloxane group bound to titanium under the formation of trimethyl silane chloride (Scheme II (3)). Alcohol reacts with trimethyl silane chloride to form small amounts of trimethyl ethoxysilane (Scheme II (4-6)). The alcohol produced during the reaction reacts with HCl to form trimethyl silane chloride, trimethyl ethoxysilane, and the polymer. These reactions were confirmed by further experiments in which bis-(trimethylsiloxy) titanium dichloride was converted into a polymer even in the presence of small amounts of water (Scheme III (1-3)). There are 3 Soviet references.

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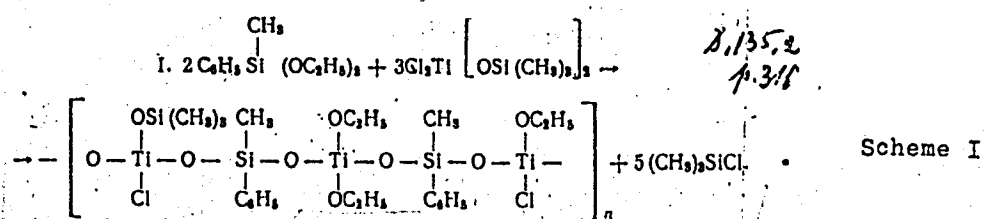
86393

The Reaction of Heterofunctional Condensation of Bis-(trimethylsiloxy) Titanium Dichloride With Phenyl-methyl Diethoxysilane

S/020/60/135/002/018/036
B016/B052

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds of the Academy of Sciences USSR)

SUBMITTED: July 6, 1960



Card 3/8

86039

15.8114

S/020/60/135/003/023/039
B016/B054.

AUTHORS: Andrianov, K. A. Corresponding Member AS USSR, and
L. I. Makarova

TITLE: Synthesis of Diatomic Alcohols of the Siloxane Series.
Synthesis of Bis(β -hydroxy-ethoxy-methyl)-polydimethyl
Siloxanes

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 3,
pp. 595 - 598

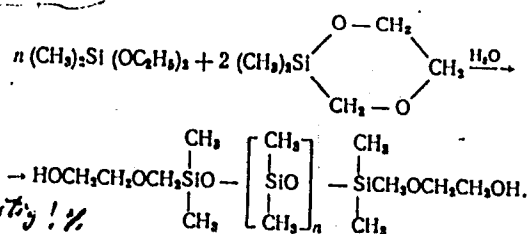
TEXT: The authors report on the synthesis of bivalent organosilicon alcohols with hydroxyl groups in the organic radicals. They succeeded in synthesizing such alcohols with 1, 2, 12, 13, 20, and 21 dimethyl siloxane members, namely bis(β -hydroxy-ethoxy-methyl)-polydimethyl siloxanes (BHPS) with a molecular weight of 360-1800. To produce such dimethyl-siloxane oligomers with β -hydroxy-ethoxy-methyl groups at the ends of the chain, the authors studied the cohydrolysis of dimethyl-diethoxy silane with a heterocyclic derivative (the synthesis of the latter is described in the authors' paper, Ref. 3) (reaction (I)).

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Synthesis of Diatomic Alcohols of the Siloxane S/020/60/135/003/023/039
Series. Synthesis of Bis(β -hydroxy-ethoxy-
methyl)-polydimethyl Siloxanes B016/B054

$(CH_3)_2SiOCH_2CH_2OCH_3$, синтез которого был описан в предыдущем сообщении (?), по реакции



little quantity !

7.15.3

1.535

(1)

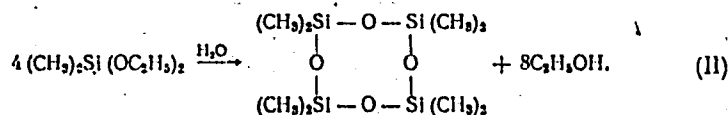
Card 12/5

86039

Synthesis of Diatomic Alcohols of the
Siloxane Series. Synthesis of Bis(β -hydroxy-
ethoxy-methyl)-polydimethyl Siloxanes

S/020/60/135/003/023/039
B016/B054

This reaction is based on the good hydrolyzability of the heterocyclic derivative. The authors made the hydrolysis in aqueous-acid medium without a solvent. The reaction proceeded according to scheme (I); it was, however, accompanied by a side reaction of the hydrolysis of dimethyl-diethoxy silane with a formation of octamethyl cyclotetrasiloxane (reaction (II)).



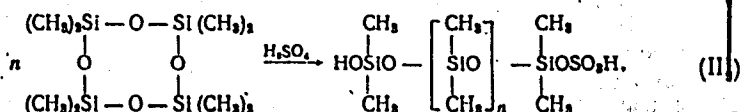
Thus, the quantitative ratio between the dimethyl-diethoxy silane used and the heterocyclic derivative was modified, which led to the formation of BHPS with about half the number of dimethyl siloxane members as would correspond to the ratio of the components used. Therefore, the authors modified the conditions of hydrolysis to reduce the side reaction by adding water according to the equations: $A = n/(n-m)$ (Ref. 4), where A is the number of dimethyl siloxane members, n the number of moles of the heterocyclic derivative, and m the mole number of water. Under these con-

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Synthesis of Diatomic Alcohols of the Siloxane S/020/60/135/003/023/039
Series. Synthesis of Bis(β -hydroxy-ethoxy- B016/B054
methyl)-polydimethyl Siloxanes

ditions, BHPS are formed with a number of dimethyl siloxane members which nearly corresponds to the number given according to the reaction. Hence, the authors conclude that the reaction exclusively proceeds according to scheme (I). The yield in BHPS attained 80%, and no polydimethyl siloxanes were formed. For the synthesis of BHPS, they also used the reaction of catalytic transformation of octamethyl cyclotetrasiloxane with H_2SO_4 . It produces linear polydimethyl siloxanes (scheme (III)).



By an adjustment of the quantitative ratio between H_2SO_4 and octamethyl cyclotetrasiloxane, the degree of polymerization can be varied within required limits. The second step of the reaction is based on a cohydrolysis of the oligomer produced according to scheme (III) with the heterocyclic derivative mentioned at the beginning. On the basis of their results, the

Card 4/5

ANDRIANOV, Kuz'ma Andrianovich; ASNOVICH, Emmanuil Zinov'yevich;
PETRASHKO, Aleksey Ivanovich; NEKHLYUDOVA, A.S., red.; SAVCHENKO,
Ye.V., tekhn. red.

[Chemistry of large molecules] Khimiia bol'shikh molekul. Moskva,
Izd-vo "Znanie," 1961. 39 p. (Narodnyi universitet kul'tury:
Estestvennonauchnyy fakul'tet, no.18) (MIRA 15:1)

1. Chlen-korrespondent AN SSSR (for Andrianov).
(POLYMERS)

ANDRIANOV, Kuz'ma Andrianovich. Prinimali uchastiye: PARKSHEYAN, Kh.R.;
ROMANOV, R.G.; SEMENKO, P.Ya.; ZABYRINA, K.I. . red.;
KALITVYANSKIY, V.I., red.; KORITSKIY, Yu.V., red.; KHVAL'KOVSKIY,
A.V., red.; EPSHTEYN, L.A., red.

[Macromolecular compounds for electrical insulation] Vysoko-
molekuliarnye soedineniia dlia elektricheskoi izoliatsii. Mo-
skva, Gos. energ.izd-vo, 1961. 327 p. (Polimery v elektroizo-
liatsionnoi tekhnike, no.1) (MIRA 15:2)
(Electric insulators and insulation) (Polymers)

37753

S/661/61/000/006/004/081
D205/D302

5.3700

11.12.50

AUTHORS: Trofimova, I. V., ~~Andrianov~~, K. A., Golubtsov, S. A.,
Turetskaya, R. A., Belyakova, Z. V., Yakusheva, T. M.,
Lobusevich, N. P. and Luzganova, M. A.

TITLE: On the regulation of the composition of products in the
direct synthesis of methyl- and ethyl chlorosilanes in
a fluidized bed

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganiches-
kikh soyedineniy; trudy konferentsii. no. 6, Doklady,
diskussii, resheniya. II Vses. konfer. po khimii i prakt.
prim. kremneorg. soyed., Len., 1958. Leningrad, Izd-vo
AN SSSR, 1961, 25-27

TEXT: Regulation of the process is one of the main problems in
preparing monomeric organosilicon compounds. The most interesting
results were obtained during the attempt to regulate the product
composition by varying the preparation procedure of the catalyst.

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X

37754

S/661/61/000/006/005/081
D205/D302

5:3700

11.1250

AUTHORS: Lobusevich, N. P., Trofimova, I. V., Andrianov, K. A.,
Golubtsov, S. A. and Belyy, A. P.

TITLE: Influence of some metal additives on the activity of
silicon-copper alloys in the synthesis of methyl chloro-
silanes

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganiches-
kikh soedineniy; trudy konferentsii. no. 6, Doklady,
diskussii, resheniye. II Vses. konfer. po khimii i
prakt. prim. kremneorg. soyed., Len., 1958. Leningrad.
Izd-vo AN SSSR. 1961, 28-31

TEXT: The influence of impurities commonly encountered in silicon
(Al, Fe, Ca) and copper (Bi, Sn, Pb) on the activity of silicon-
copper alloys used in methyl chlorosilane synthesis was investiga-
ted. Two series of alloys were prepared: 1) From purified Si with
less than 0.2% of impurities; 2) from Kp-1 (Kr-1) silicon with 2%
impurities. These alloys, notwithstanding the identical procedure

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37759
S/661/61/000/006/016/081
D205/D302

5.3700.

AUTHORS: Popeleva, G. S., Trofimova, I. V., Andrianov, K. A.
and Golubtsov, S. A.

TITLE: Study of vinyl chlorosilane synthesis

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh soedineniy; trudy konferentsii, no. 6, Doklady, diskussii resheniye. II Vses. Konfer. po khimii i prakt. prim. kremneorg. soyed., Len. 1958. Leningrad. Izd-vo AN SSSR. 1961, 90-94

TEXT: During the investigation of the reaction $3\text{CH}_2 = \text{CHCl} + \text{SiCH}_2 = \text{CHSiCl}_3$ it was found that the catalyst prepared from precipitated CuO , Si powder and a liquid glass binder was the most active. 3 methods of contacting were tried: (1) Stationary bed of pelletized catalyst (2 - 3 mm pellets); (2) an agitated powder bed; (3) a fluidized bed. The first method gave good results when using anhydrous FeCl_3 as an activator. The second method allowed the low-

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D205/D302

Study of vinyl ...

ering of the temperature from 460 to 420°C. The vinyl trichlorosilane yield was 33% and the output 10 - 15 g/hour/kg of catalyst. The third method resulted in a reduction of the contact time by a factor of 12 and a corresponding considerable increase in temperature. The yield of vinyl trichlorosilane was reduced, as the side reactions were enhanced, to ~26%. In contrast to the synthesis of methyl, ethyl and phenyl chlorosilanes where the best results are obtained in the fluidized bed, this method does not provide the contact times necessary for synthesis of vinyl chlorosilanes. As an alternative to the above reaction, the reaction $\text{HSiCl}_3 + \text{CH}_2 = \text{CHSiCl}_3 + \text{HCl}$ is proposed. This reaction was investigated, yields of 65% being obtained at 500°C with a contact time of 35 seconds. In the synthesis of methyl vinyl dichlorosilane by the reaction $\text{CH}_3\text{SiHCl}_2 + \text{CH}_2 = \text{CHCl} \rightarrow \text{CH}_3(\text{CH}_2=\text{CH})\text{SiCl}_2 + \text{HCl}$, the optimum conditions ensuring a 55% yield were 540°C and a contact time of 30 seconds. Thus the condensation of hydrochlorosilanes with vinyl

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ANDRIANOV, K. A.

S/661/61/000/006/019/081
D205/D302

AUTHORS: Tarasova, A. S., Petrov, A. D., Andrianov, K. A., Golubtsov, S. A., Ponomarenko, V. A., Cherkayev, V. G., Zadorozhnyy, N. A. and Vavilov, V. V.

TITLE: Continuous addition of hydrochlorosilanes to unsaturated compounds

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh soyedineniy; trudy konferentsii, no. 6, Doklady, diskussii resheniye. II Vses. Konfer. po khimii i prakt. prim. kremneorg. Soyed., Len. 1958. Leningrad, Izd-vo AN SSSR. 1961, 90-100

TEXT: For practical application of the addition reactions of methyl dichlorosilane, ethyl dichlorosilane and trichlorosilane to liquid and gaseous unsaturated compounds an apparatus was designed and optimum conditions of synthesis were established. The chlorosilane and the gas are fed into a reactor. The products are discharged via a cooler into a receiver equipped with a reflux. Dur-

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D205/D302

Continuous addition of ...

ing the reaction the reactor and cooler are cooled by water, the receiver and the reflux by brine. The arrangement was tested on the reaction of ethylene with methyl dichlorosilane and ethyl dichlorosilane. The experiments have shown that in the 35 - 200°C temperature range the reaction is unchanged giving a 65 - 75% yield. No by-products are formed and the output is high (> 6 kg of methyl ethyl dichlorosilane/hr/l of reactor volume). The process is amenable to automation owing to its insensitivity to temperature changes. There are 1 figure and 1 table.

Card 2/2

S/661/61/000/006/036/031
D202/D302

AUTHORS: Alashkevich, M. L., Leznov, N. S., Yumakova, A. Ye. and Andrianov, K. A.

TITLE: Physico-mechanical properties of linear polydiethylsiloxanes

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh soyedineniy; trudy konferentsii. no. 6: Doklady, diskussii, resheniye. II Vses. konfer. po khimii i prakt. prim. kremneorg. soyed., Len., 1958. Leningrad, Izd-vo AN SSSR, 1961, 171-172

TEXT: A supplement to a previous report in no. 2, p. 20, of this publication. The authors compare the properties of polymethylphenylsiloxanes with those of polydiethylsiloxanes used as high-vacuum pump fluids. No experimental details are given. It was found that the first compounds have marked advantages over the second, although cyclic polymers, formed during their synthesis, unfavorably affect the thermal stability of both. ✓

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3/661/61/000/006/038/031
D202/D302

AUTHORS: Kuznetsova, A. G., Andrianov, K. A. and Zhinkin, D. Ya.
TITLE: On the co-hydrolysis of diethyldichlorosilane and phenyl-trichlorosilane
SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh soyedineniy; trudy konferentsii. no. 6: Doklady, diskussii, resheniye. II Vses. konfer. po khimi i prakt. prim. kremneorg. soyed., Len., 1958. Leningrad, Izd-vo AN SSSR, 1961, 175-179

TEXT: A discussion on a previous report (no. 2, p. 33, this publication) in which the authors and P. V. Davydov (Moscow), N. S. Ieznov (Moscow), N. N. Sokolov (VEI, Moscow) and A. V. Karlin (VNIISK, Leningrad) took part. The role of solvents, especially that of ethyl-ether, in the co-hydrolysis process of the above-mentioned compounds and the unfavorable effect of methyl-trichlorosilane admixtures in dimethyldichlorosilane used in the process were discussed.

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S/061/61/000/006/040/081
D202/D302

AUTHORS: Dzhemel'skaya, S. I., Andrianov, K. A. and Petrashko,
Yu. K.

TITLE: The catalytic polymerisation of polydimethylsiloxanes

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh soedineniy; trudy konferentsii. no. 6: Doklady, diskussii, resheniye. II Vses. konfer. po khimii i prakt. prim. kremneorg. soved., Len., 1958. Leningrad, Izd-vo AN SSSR, 1961, 180-181

TEXT: A discussion on a previous report (no. 2, p. 45, this publication) between K. A. Andrianov, N. N. Sokolov (VEI, Moscow), A. V. Karlin (VNIISK, Leningrad) and M. C. Voronkov (IKhS, AS USSR). The catalytic effect of NaOH on its thermal stability (at 300°C), as well as the possible use of quaternary ammonium bases as catalysts and the inefficiency of acidic catalysts were discussed.

ASSOCIATION: Vsesoyuznyy elektrotekhnicheskiy institut im. V.I. Lenina, Moskva (All-Union Electrotechnical Institute im. V. I. Lenin, Moscow) ✓

Card 1/1

37765

S/661/61/000/006/049/081
D244/D302

5.3700

AUTHOR: Andrianov, K. A.

TITLE: On the more important trends in the development of organosilicon compounds

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh soyedineniy; trudy konferentsii; no. 6: Doklady, diskussii, resheniye. II Vses. konfer. po khimii i prakt. prim. kremneorg. soyed., Len. 1958. Leningrad, Izd-vo AN SSSR, 1961, 213-216

TEXT: This is a discussion in which N. P. Orlov (IKhS AN SSSR, Leningrad), Ye. M. Oparina (Moscow), V. I. Pakhomov (NIIPM, Moscow), S. N. Borisov (VNIIDK, Leningrad), A. I. Dintses (Moscow) and P. P. Nikotin ("Sevkabel" Plant, Leningrad) took part. The author disclosed that the work on the synthesis of polymers with Si-O-Al links is directed toward preparing rigid and elastic polymers. The new polymers do not liquefy at 500 - 600°C, and dissolve in benzene, toluene and certain other solvents. They are good hardeners

Card 1/2

S/661/61/000/006/049/031
D244/D302

On the more important ...

for the silicon organic resins. The plastic masses can be easily moulded by usual methods and can withstand working temperatures of 400 - 420°C. In addition, polyorgano-aluminosiloxanes are of interest from the point of view of the study of silicates. Introduction of Al into siloxane structure gives soluble molecules, the structure of which is akin to that of silicates. The molecular weight is about 40,000. Preliminary work indicated that inclusion of certain solvents into the polymers gives optically transparent materials retaining the properties of rigid polymers. The disadvantage of such systems is their high brittleness. Investigation of polymers containing Ti indicated that the bond Si-O-Ti is very stable to hydrolysis. Only 3.5% of the titanosiloxane polymer was hydrolysed with 20 - 30% HCl for 10 hours, whilst kaolin is completely hydrolyzed under these conditions after 3 - 4 hours. Practical utilization of the titanium polymers is difficult because of instability of the Ti-C bond. It is, therefore, necessary to have C-O-Ti links. .

Card 2/2

S/661/61/000/006/050/081
D235/D302

AUTHORS: Kozlovskaya, L. N., Glukhova, A. I., Andrianov, K. A.
and Kaluzhenina, K. F.

TITLE: Thermal stability of materials based on poly-dimethyl-
siloxanes

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganiches-
kikh soyedineniy; trudy konferentsii, no. 6: Doklady,
diskussii, resheniye. II Vses. konfer. po khimii i
prakt. prim. kremneorg. soyed., Len. 1958. Leningrad,
Izd-vo AN SSSR, 1961, 216-220

TEXT: A supplement to the above paper (this publication, no. 2,
p. 95). The authors report on materials formed from polydimethyl-
siloxanes and fluoro-organic polymers. Such materials can be used
at 350°C for 300 hours and at 300°C there is practically no change
in the properties after 1,000 hours. After service at 300 - 350°C
the mechanical strength is 100 - 110 kg/cm² and the specific elon-
✓

Card 1/3

S/661/61/000/006/050/081
D235/D302

Thermal stability of ...

gation 80 - 100%, the resistance to breakdown after the action of oil for 200 hours at 200°C falls by 40 - 50% and swelling amounts to 20 - 25%; shrinkage after heat treatment is about 5%. The material can be used for packing, sealing, etc.; because it forms few volatile compounds it will find application in vacuum technology. The paper is discussed by the authors and A. L. Klebanskiy (VNIISK, Leningrad), A. A. Berlin (Moscow), V. I. Pakhomov (NIIPM, Moscow) and N. Nudel'man (NIIRP, Moscow). The following topics are discussed: Vulcanization of the polymers; toxicity of the material; the immediate formation at room temperature of polymer fragments on rolling; properties; the mechanism for the formation of polymer fragments by destruction of Teflon and polydimethylsiloxane; and the amount of filler for the material. Vulcanization takes place by breakdown of polymer chains, the formation of benzoyl peroxide and subsequent recombination of the macromolecules; it takes place with respect to fragments of polydimethylsiloxane and not with respect to the fluoro-polymer. The number of volatile compounds is negligible and the material does not cause metallic corrosion. The

Card 2/3

S/661/61/000/005/051/081
D235/D302

AUTHORS: Zhdanov, A. A. and Andrianov, K. A.

TITLE: Polyorgano-metallo-siloxanes and polyorgano-siloxy-metalloxanes

SOURCE: Khimiy i prakticheskoye primeneniye kremneorganicheskikh soyedineniy; trudy konferentsii, no. 6: Doklady, diskussii, resheniye. II Vses. konfer. po khimii i prakt. prim. kremneorg. soyed., Len. 1958. Leningrad, Izd-vo AN SSSR, 1961, 220-224

TEXT: A discussion of the above paper (this publication, no. 2, p. 100) between the authors and N. F. Orlov (IKhS AN SSSR, Leningrad), S. N. Borisov, (VNIISK, Leningrad) and M. G. Voronkov (IKhS AN SSSR, Leningrad). The following points are discussed: Thermal and hydrolytic stability of the bonds silicon-oxygen-metal; introduction of the elements magnesium and zinc into the siloxane structure; the formation of poly-diethyl-alumina-siloxane; reasons for the increase in thermal stability obtained by the authors; thermal

Card 1/3

S/661/61/000/006/051/031
D235/D302

Polyorgano-metallo-siloxanes ...

and hydrolytic stability of poly-organo-titanium siloxanes. The thermal stability of the bonds Si-O-M is fairly high and a compound such as $(R_2SiO)_4Ti$ is hydrolyzed only very slowly by water. Magnesium reacts like aluminum with hydroxyl containing silicon compounds to give hydrogen and the siloxane polymer containing magnesium. Reference is made to a patent by Viberg and Katnslev where poly-diethyl-alumina-siloxane is obtained by reacting the metal with diethyl siloxane at $310^{\circ}C$; the authors only obtained a 1.5 - 2% yield by such a reaction. Alkaline hydrolysis of dimethyl-siloxane with aluminum chloride in the ratio Si-Al of 3:1 to 45:1 leads to the formation of gel-like polymers and in the ratio Si:Al of 60:1 to 100:1 to co-polymers similar to poly-dimethyl-siloxane rubbers, but the exterior is frequently gummy. Thermal stability of poly-organo-titanium-siloxanes is considerably higher than for the aluminum compounds. The bond Si-O-Ti has higher thermal stability than the compounds with a siloxane bond due to the effect of oxygen on Si-C under the action of titanium. The hydrolytic stability depends on the nature of the radical connected to silicon and the molecular structure. Derivatives from elements of group V possess the greatest

Card 2/3

Polyorgano-metallo-siloxanes ...

S/661/61/000/006/051/031
D235/D302

stability, as compared with derivatives from groups III and IV, but there is no quantitative information concerning this.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR, Moskva (Institute of Elemental Organic Compounds, Academy of Sciences, USSR, Moscow)

Card 3/3

✓

5.3700

37766

S/661/61/000/006/052/031
D235/D302

AUTHORS: Mindlin, Ya. L., Leznov, N. S. and Andrianov, K. A.

TITLE: Synthesis of polymethyl-siloxanes with hydroxyl groups
in the organic radical

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh
soyedineniy; trudy konferentsii, no. 6: Doklady, diskus-
sii, resheniye. II Vses. konfer. po khimii i prakt. prim.
kremneorg. soyed., Len. 1958. Leningrad, Izd-vo AN SSSR,
1961, 224-226

TEXT: A supplement to the above paper (this publication, no. 2,
p. 127). The authors report on the exceptional antifoam properties
of poly-methyl-siloxanes with a hydroxyl group in the organic radi-
cal. Such a compound depresses foam formation during fermentation
of a number of antibiotics and the expenditure of the antifoam agent
is only a hundredth or thousandth part of a percent of the volume
of the fermentation medium. Such an antifoam agent, containing 5%
hydroxyl groups, in the form of a 10 - 15% solution in white spirit

Card 1/2

15.8170

37775

S/661/61/000/006/068/081
D247/D302

AUTHORS: Konstantinova, N. G., Zhdanov, A. A., Andrianov, K. A.,
Sharov, M. Ya., Kyutner, M. A. and Zakharov, A. A.

TITLE: Thermostable lacquer coatings based on silico-organic
polymers

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganiches-
kikh soyedineniy; trudy konferentsii, no. 6: Doklady,
diskussii, resheniye. II Vses. konfer. po khimii i
prakt. prim. kremneorg. soyed., Len. 1958. Leningrad,
Izd-vo AN SSSR, 1961, 296-299

TEXT: A study was made of the thermostability of several lacquer-
painted materials on the basis of different film-forming substan-
ces. The silico-organic resin K-47 was modified by the use of orga-
nic polymers to give a hard, cold-drying coat of increased thermo-
stability. The metallic surface and its preparation was found to
have a great influence on the adhesion, the protective properties
and the thermostability of the coatings. In the discussion, the

Card 1/2

S/661/61/000/006/069/081
D247/D302

AUTHORS: Fromberg, M. B., Andrianov, K. A. and Zabyrina, K. I.

TITLE: Block polymers from polyorganic silicones for electrical insulating coatings for air drying

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh soyedineniy; trudy konferentsii, no. 6: Doklady, diskussii, resheniye. II Vses. konfer. po khimii i prakt. prim. kremneorg. soyed., Len. 1958. Leningrad, Izd-vo AN SSSR, 1961, 299-300

TEXT: The text is in the form of a discussion in which A. F. Moiseyev (Moscow) took part. Some thermal and mechanical properties of the polymers (thermostable up to 200°C) are mentioned, and indirect evidence for their block structure is given.

ASSOCIATION: Vsesoyuznyy elektrotekhnicheskiy institut im. V. I. Lenina, Moskva (All-Union Electrotechnical Institute im. V. I. Lenin, Moscow) ✓

Card 1/1

88640

S/110/61/000/001/001/023
E194/E455

15.8340

AUTHORS: Andrianov, K.A., Corresponding Member AS USSR,
Golubenko, M.A., Engineer

TITLE: Cast Insulation Based on Epoxide Resins and
Polyorganosiloxanes

PERIODICAL: Vestnik elektropromyshlennosti, 1961, No.1, pp.1-3

TEXT: This article describes cast insulation which has been developed on the basis of epoxide resins and polyorganosiloxanes. Polyorganosiloxanes have good electrical and thermal but poor mechanical properties; they can, however, be combined with certain organic polymers to form block polymers. In the case of polyorganosiloxanes the reactive groups are hydroxyls and esters and in the epoxide resins they are epoxide and hydroxyl groups. Epoxide resin grade Э-37 (E-37) was selected as basis because besides having good casting properties it has a long hardening time. Polyorganosiloxanes of various compositions and structures may be derived from silicon-organic monomers: methyl phenyl-dichlorsilane and dimethyldichlorsilane. The content of hydroxyl groups in the polyorganosiloxane is 1 to 3% and of ethoxyl groups from 1 to 6%. The epoxide resins are combined with polyorgano-
Card 1/4

88640

S/110/61/000/001/001/025

E194/E455

Cast Insulation Based on Epoxide Resins and Polyorganosiloxanes

siloxanes either in a solvent or in the fluid condition and the resulting compounds contain from 10 to 80% of polyorganosiloxanes. The resulting compounds are uniform transparent products ranging in colour from light yellow to dark brown. The compounds become liquid at 80 to 100°C and can be maintained at this temperature for a considerable time without change. Their method of use is simple and similar to that of epoxide compounds. Materials that can be used as hardeners for EK (EK) compounds are phthalic or maleic anhydrides, amines, polyalumino-organosiloxanes and others. The quantity of hardener depends on the content of epoxide groups in the compound and usually ranges from 5 to 20% by weight. The compounds are hardened at a temperature of 100 to 200°C, which usually takes several hours. Then the cast compounds are heat-treated at 150 to 200°C for 24 to 48 hours. This heat treatment improves the dielectric properties. The physical properties of the compounds depend on the content and structure of the polyorganosiloxanes. Mineral fillers may be used. The greater the content of polyorganosiloxanes the greater the plasticity. Shrinkage of EK compounds containing 20 to 30% of polyorgano-

Card 2/4

88610
S/110/61/000/001/001/023
E194/F455

Cast Insulation Based on Epoxide Resins and Polvorganosiloxanes

five days in water. The dielectric properties mainly depend on those of the epoxide resin grade E-37 used in preparing the compounds. There was little increase in dielectric loss with voltage up to 35 kV. Compound EK-20 with quartz sand as filler had a power factor of 0.013 at 20°C and 0.040 at 130°C. After ageing at 200°C for 600 hours the power factor at 20°C rose from 0.0023 to 0.0032. A tropical humidity test of more than 500 hours has practically no effect on the electrical properties. Compound EK-20 has been used for impregnating and "potting" non-rotating components operating at temperatures ranging from -60 to +200°C. There are 2 figures, 5 tables and 4 references: 3 Soviet and 1 non-Soviet.

SUBMITTED: March 11, 1960

Card 4/4

89919

Comparative properties of organo...

S/191/61/000/002/007/012
B124/B204

in air was compared. Fig. 1 shows the dependence of the viscosity of the compounds I and II upon the heating time at 250°C. Fig. 2 shows the change in viscosity of the compounds III and IV with the heating time at 200°C. Fig. 1 shows that the viscosity in the case of heating at 250°C grows more quickly with compound I than with compound II. The results obtained by the analysis of the chemical composition of the liquids investigated (Table) show that in the case of heating, the molecular weight and the silicon content in compounds with a methyl siloxane chain (I and III) increase more quickly than in compounds with the siloxane chain (II and IV) which characterizes the destruction processes in the organic part of the molecule. The organomethyl siloxanes (I and III) are also less resistant to thermooxidation. The substitution of the oxygen of the methylene group in the molecule chain of organosiloxane weakens the shielding effect of the siloxane bond in comparison to the silicon-organic frame groups, which leads to a decrease of thermooxidation stability of the frame groups. The temperature coefficient of viscosity grows in the interval of from +50 to -30°C considerably in the case of substitution of oxygen in the siloxane

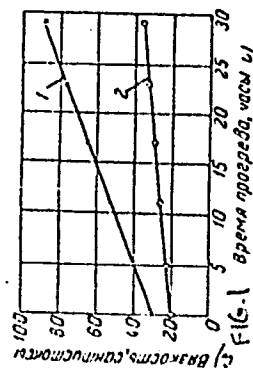
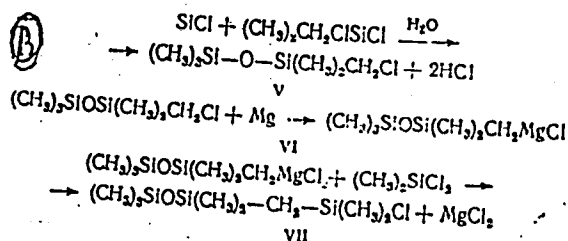
Card 2/8⁴

89919

Comparative properties of organo...

S/191/61/000/002/007/012
B124/B204

chain by the group $-\text{CH}_2-$; in compound I it equals 330 and in compound II 35 (Fig. 3). Compound III shows the same temperature dependence of viscosity. The absolute value of the viscosity coefficient in the temperature interval of from $+50$ to -50°C is, however, considerably lower, in compound III it amounts to 12.9 and in compound IV to 7.65 (Fig. 4). As initial compounds, chlorosilane, dimethylchloromethylchlorosilane, dimethyldichlorosilane and methylphenyldichlorosilane were taken. The compound with a methylenesiloxane chain is obtained by means of the reactions:



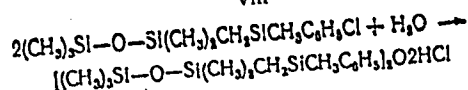
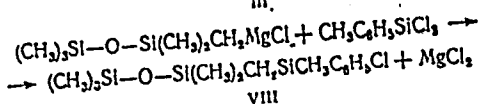
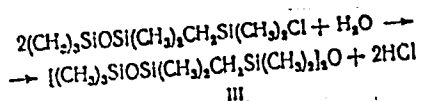
Card 3/8

89919

S/191/61/000/002/007/012
B124/B204

Comparative properties of organo...

Magnesium-organic compound VI is not only formed in sulfuric ether but also in toluene, however, the reaction to the compounds VII and VIII in toluene, does not develop quantitatively in toluene also if the reaction time of 8 (in ether) is extended to 13 hr in the reaction with dimethyl-dichlorosilane and to 30 hr in the reaction with methylphenyldichlorosilane. There are 4 figures, 1 table, and 3 non-Soviet-bloc references.



Legend to Fig. 1: Change in viscosity in heating up to 250°C; 1 - compound I; 2 - compound II; a) viscosity, centistokes; b) heating time, hr.

Card 4/8

5.3700

2209, 1164

20939

S/062/61/000/003/005/013
B117/B208

AUTHORS:

Andrianov, K. A. and Nikitenkov, V. Ye.

TITLE:

Synthesis of organosilicon compounds with phenylene
siloxane chains of the molecules

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, no. 3, 1961, 441-444

TEXT: The authors studied the hydrolysis of 1-methyl-phenyl chloro silane-
4-phenyl dichloro silane benzene and 1,4-bis-(phenyl dichloro silane)-
benzene in an aqueous ether medium. Hydrolysis of 1-methyl-phenyl chloro
silane-4-phenyl dichloro silane benzene takes place in an acid medium to
form a crystalline compound in a yield of 99.1 % according to the scheme;

Card 1/6

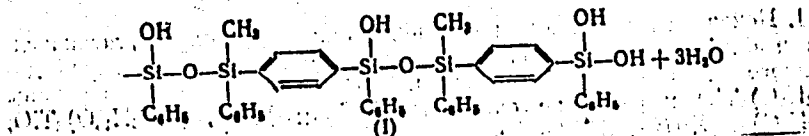
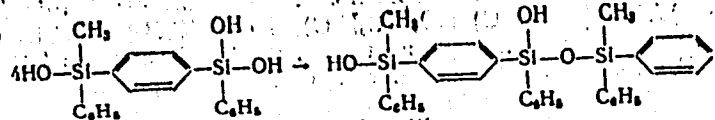
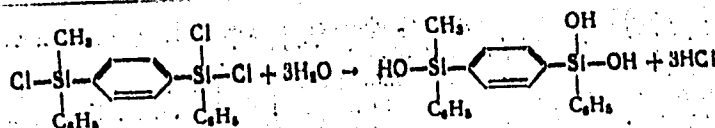
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B117/B208

Synthesis of organosilicon...

1)



This compound was found to contain 7.5 % hydroxyl groups. The molecular weight is 1329. The elementary composition corresponds to compound (I). Ultrared spectra show frequencies that can be ascribed to the following bonds: CH_3-Si , $\text{C}_6\text{H}_5-\text{Si}$, C_6H_4 , $\text{HO}-\text{Si}$. The vibrational frequencies of

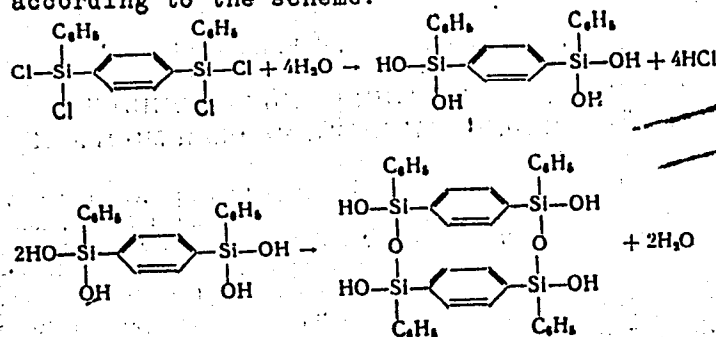
Card 2/6

20939

S/062/61/000/003/005/013
B117/B208

Synthesis of organosilicon...

Si-O-Si bonds in the range of 1075 cm^{-1} correspond to a linear compound. The resultant compound is well soluble in acetone, benzene, chloro-benzene, toluene, carbon tetrachloride, sulfuric ether, dioxane, acetylene tetrachloride, chloroform, cyclohexanone, aniline, and cresol; insoluble in methyl and ethyl alcohols, in petroleum ether and water. The melting point of this compound is $84^{\circ}\text{--}85^{\circ}\text{C}$. Water is readily split off when heated, and thus a complicated compound results. During the hydrolysis of 1,4-bis-(phenyl dichloro silane)benzene a cyclic, low-molecular compound, bis-[1,4-bis-(phenyloxy-silane)benzene]cyclodioxide results in an acid medium with a 83.5 % yield according to the scheme:




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S/062/61/000/003/005/013
B117/B208

Synthesis of organosilicon...

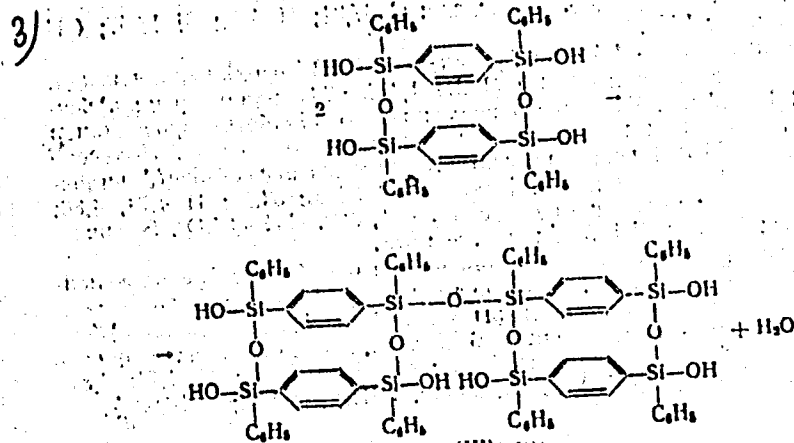
Infrared spectra of this compound show frequencies to be assigned to the C_6H_5-Si , , $HO-Si$ bonds. Elementary composition and molecular weight correspond to compound (II). This compound is soluble in dioxane, acetone, acetylene tetrachloride, sulfuric ether, aniline, cyclohexanone, chloroform, methyl and ethyl alcohols in the cold, in benzene, toluene, chloro-benzene and cresol, when heated, insoluble in carbon tetrachloride, petroleum ether, 1,2-dibromo methane, cyclohexane, octamethyl cyclotetra-siloxane, and water. It melts at $93^{\circ}-104^{\circ}C$ which indicates that the polycondensation of this compound occurs during heating. In boiling benzene, this condensation yields a polymer with the molecular weight 3770. Bis-[1,4-bis-(phenyloxy silane)benzene]-cyclodioxide was found to condense on prolonged standing in the form of 50 % ether-toluene solution, and to lose its solubility. Ultimate analysis and infrared spectra show that the condensation of this compound yields a dicyclic compound according to the scheme:

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B117/B208

Synthesis of organosilicon...



Vibrational frequencies of the $\text{C}_6\text{H}_5-\text{Si}$, C_6H_4 , $\text{HO}-\text{Si}$ bonds were found. The absorption bands of $\text{Si}-\text{O}-\text{Si}$ in the range of $1015-1080 \text{ cm}^{-1}$ are more

Card 5/6

20939

S/062/61/000/003/005/013
B117/B208

Synthesis of organosilicon...

intense than in compound (II) in the range of 1080 cm^{-1} . The number of hydroxyl groups in compound (III) decreases compared with (II). There are 3 Soviet-bloc references.

ASSOCIATION: Vsesoyuznyy elektrotekhnicheskiy institut im. V. I. Lenina
(All-Union Electrotechnical Institute imeni V. I. Lenin)

SUBMITTED: December 26, 1959

Card 6/6

22738

158116 22 09

S/191/61/000/006/003/005
B101/B215

AUTHORS: Andrianov, K. A., Krasovskaya, T. A., Ponomareva, T. I.

TITLE: Catalytic transformations of a mixture consisting of the products of cohydrolysis of methylphenyl dichlorosilane and trimethylchlorosilane

PERIODICAL: Plasticheskiye massy, no. 6, 1961, 21-24

TEXT: The cohydrolysis following the formula is said to be a suitable method for obtaining liquid polyorganosiloxanes: $2R_3SiX + nR'_2SiX_2 + (n+1) \cdot H_2O \longrightarrow R_3SiO[SiR'_2O]_nSiR_3 + 2(n+1)HX$ (I). Besides, however, a parallel condensation of the individual hydrolysis products takes place under the formation of cyclic compounds: $mR'_2SiX_2 + mH_2O \longrightarrow [R'_2SiO]_m + 2mHX$ (II) and of disiloxane: $2R_3SiX + H_2O \longrightarrow R_3SiOSiR_3 + 2HX$ (III). To convert cyclic compounds and disiloxane into linear compounds, the mixture of cohydrolysis is treated with various catalysts. As to polymethylsiloxanes, these reactions have already been studied. In the present paper the action

Card 1/2
3

Catalytic transformations of a ...

22738
S/191/61/000/006/003/005
B101/B215

of catalysts on the cohydrolysis mixture of polymethyl-phenyl siloxanes has been studied. The action of H_2SO_4 , KOH, $FeCl_3 \cdot 6H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, and natural aluminosilicate (treated with HCl) upon the products of cohydrolysis of methyl-phenyl dichlorosilane and trimethyl chlorosilane (molar ratio of 5:2) has been examined. Cohydrolysis took place at 60°C. The product was neutralized, and the content of Si and C_6H_5 in the fraction 180-290°C was determined. Fig. 1 shows the change of viscosity under the action of catalysts; Table 1 gives the analysis of the products of catalytic transformation. The fact that viscosity at first increases rapidly when using KOH is explained by the intensive polymerization of cyclic compounds. No constant viscosity was attained for aluminosilicate, and the formation of benzene, i.e., separation of the phenyl radical from siloxane, was observed. With $FeCl_3$ and $Al_2(SO_4)_3$, the cyclic compounds were not completely rearranged at 20°C. A temperature increase to 60°C accelerated the reaction but then separation of phenyl radicals occurred. With 90% H_2SO_4 constant viscosity was attained after 4 hr. Here, complete rearrangement occurred. According to its molecular weight, the polymer

Card 2/4
3

22738

S/191/61/000/006/003/005

B101/B215

Catalytic transformations of 'a ...

corresponded to nonamethyl-triphenyl pentasiloxane. With 80% H_2SO_4 , constant viscosity was only attained after 18 hr; with 40 and 60% acid, viscosity increased continuously and the content of cyclic compounds was only slightly reduced. 94.6% acid caused the formation of linear polymers, but led to the separation of phenyl radicals. Table 3 gives the results obtained with 90% H_2SO_4 at various temperatures and various amounts of catalysts. As regards their activity, the catalysts examined range in the following order: $H_2SO_4 > KOH > FeCl_3 \cdot 6H_2O > Al_2(SO_4)_3 \cdot 18H_2O > \text{aluminosilicate}$. There are 3 figures, 3 tables, and 6 references: 1 Soviet-bloc and 5 non-Soviet-bloc. The two most important references to English-language publications read as follows: D. F. Wilcock, J. Am. Chem. Soc., 69, 477 (1947); R. N. Lewis, J. Am. Chem. Soc., 70, 1115 (1948).

Card 3/3

24747

S/191/61/000/007/005/010

B101/B215

Catalytic polymerization of...

was successful with the use of both acids and lyes as catalysts. At first, solubility was not reduced during polymerization, then gel formation occurred. It was found that polyalumino-phenyl cyclosiloxane in the presence of 1 % of NaOH at 120°C polymerizes much more quickly (gel formation within 9 hr, viscosity of the 10 % solution in toluene: 1.9) than polyphenyl cyclosiloxane (gel formation after 15 hr; viscosity: 2.64). Polyalumino-ethyl cyclosiloxane polymerized already after 7 hr, and polyalumino-phenylmethyl cyclosiloxane after 3 hr. In the presence of 1 % of ethyl sulfuric acid, the polymerization of polyalumino-phenyl cyclosiloxane at 120°C took place even more quickly than in the presence of NaOH: gel formation set in after 2 hr, and the relative viscosity increased from 1.45 to 3.91. The polymerization of alumino-organocyclosiloxane takes place gradually by precipitation of gel-forming particles. The chemical composition of the gel differs only little from that of the soluble portion of the polymer. The infrared spectra before and after polymerization showed differences only in the region of the 1060-1115 cm⁻¹ band which corresponds to the Si-O bond. The maximum of this band is shifted toward higher values. It is concluded that the polymerization is initiated by the opening of cycles and formation of cross-linked polymer molecules with a marked structure. There are 1 table and 3 Soviet-bloc references.

Card 2/2

152170

25214

S/062/61/000/007/OC4/009
B117/B215

AUTHOR: Zhdanov, A. A., Andrianov, K. A., and Bogdanova, A. A.

TITLE: Reaction of aluminum chloride with dialkyl cyclosiloxanes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 7, 1961, 1261 - 1266

TEXT: The interaction of aluminum chloride with dimethyl- and diethyl cyclosiloxanes was investigated in a study of the methods of producing polyalumo-organosiloxanes. A flask with mixer, thermometer, recoler, and cooling vessels for collecting the reaction products were used for the experiments. It was found that aluminum chloride reacts easily with dimethyl- and diethyl cyclosiloxanes at equimolecular ratios. Crystalline reaction products are formed which are quantitatively sublimated in vacuo. In the examination of the reaction mixture obtained by reaction between octamethyl cyclotetrasiloxane and aluminum chloride (mixing time: 10 hr at 120°C), the following reaction products were isolated: 1,3-dichloro tetramethyl disiloxane, boiling point: 32° - 36°C (10 mm); 1,5-dichloro hexamethyl trisiloxane, boiling point: 72° - 75°C (10 mm); 1,7-dichloro octamethyl tetrasiloxane, boiling point: 90° - 95°C (10 mm); a

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X

25214

S/062/61/000/007/004/009
B117/B215

Reaction of aluminum chloride ...

1,3-dichloro tetraethyl disiloxane, boiling point: 85°C - 90°C (10 mm);
1,5 dichlorohexaethyl trisiloxane, boiling point: 124°C - 131°C (10 mm);
1,4-dichloro octaethyl tetrasiloxane, boiling point: 131°C - 145°C
(10 mm); a crystalline substance which is sublimated at 225°C - 233°C ,
melting point: 112°C (unstable), of the empirical composition
 $\text{C}_{16}\text{H}_{40}\text{O}_6\text{Cl}_5\text{Si}_4\text{Al}_3$. The structures of the crystalline substances are
similar in both cases. An identical, crystalline substance of the
above composition and highest polydiethyl siloxanes were obtained in
the reaction between aluminum chloride and hexaethyl cyclotrisiloxane
(mixing time: 5 hr at 80°C). Conclusion: Rupture of the cycle takes
place in the interaction of aluminum chloride and the above cyclic
dialkyl siloxanes, and α -chloro- ω -dichloro aluoxymethyl polysilox-
anes are formed. The latter then separate α , ω -dichloro polysiloxanes
and form cyclic compounds: 1-chloro-3,3,5,5-tetramethyl cycloalumo-
disiloxane and 1-chloro-3,3,5,5-tetraethyl cycloalumodisiloxane.
These compounds were isolated and characterized in the form of com-
plexes with aluminum chloride. There is 1 non-Soviet-bloc reference.

Card 3/4

25214
Reaction of aluminum chloride ...

S/062/61/000/007/004/009
B117/B215

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Adademii nauk
SSSR (Institute of Elemental Organic Compounds of the
Academy of Sciences USSR)

SUBMITTED: September 26, 1960

Card 4/4

15.8170

25215

S/062/61/000/007/005/009
B117/B215AUTHOR: Andrianov, K. A., and Delazari, N. V.TITLE: Reaction of cohydrolysis of bis-(methyl-dichloro silyl)-
benzene with trimethyl chlorosilanePERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 7, 1961, 1266 - 1269

TEXT: The cohydrolysis of bis-(methyl-dichloro silyl)-benzene with trimethyl chlorosilane in a molecular ratio of 1:5 was studied. Sulfuric ether and ammonia acceptor were used as medium. 24 ml of 15 % NH_4OH , 100 g of ice, and 40 ml of sulfuric ether were filled into a 500 ml glass with mixer, thermometer, and dropping funnel. A chloride mixture consisting of 7.2 g of trimethyl chlorosilane and 5 g of bis-(methyl-dichloro silyl)-benzene was added dropwise at -8°C . It was left unmixed. After separation of the layers and distillation, 3.83 g of a yellow, thick, viscous liquid was obtained, (83.5% of the theoretical amount): C 46.10; H 7.29; Si 28.56; OH groups 5.46%; molecular weight: 518. $\text{C}_{22}\text{H}_{40}\text{Si}_6\text{O}_6$.

In the second experiment, 15% NH_4CH_3 , 100 ml of ice water, and 200 ml of
Card 1/6

Reaction of cohydrolysis ... 25215

S/062/61/000/007/005/009
B117/B215

sulfuric ether were filled into a 1 l glass with mixer, dropping funnel, and thermometer. A chloride mixture consisting of 14.5 g trimethylchlorosilane and 10.1 g bis-(methyl-dichloro silyl)-benzene was added dropwise at -2 °C and mixed for 30 minutes. After separation of the layers and distillation, 7.47 g (88.6 % of the theoretical amount) of a yellow, very thick, viscous liquid was obtained: C 46.96; H 6.64; Si 29.89; OH groups: 4.44 %, molecular weight: 787. $C_{30}H_{50}Si_8O_8$. In the third experiment, 300 ml of dry benzene and 19 g of trimethyl hydroxy silane were filled into a 500 ml three-necked flask. During cooling to -5 °C by means of ice, 13.5 g of bis-(methyl-dichloro silyl)-benzene were added dropwise to 50 ml of dry benzene in ammonia current. A white deposit formed. After dropwise addition of the chloride, ammonia was passed through for another 30 min. The mixture was then kept at 30 °C for 2 hr. A fraction with a boiling point of 217 - 220 °C (2 mm) was isolated from the filtered and distilled residue; 2.2 g; 6.97 % of the theoretical amount;

n_D^{20} 1.4610; d_4^{20} 0.9680; C 46.95; H 8.78; Si 31.79 %. $C_{28}H_{56}Si_8O_6$.

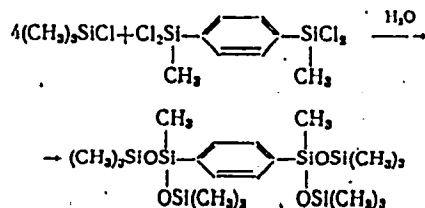
Card 2/6

Reaction of cohydrolysis ...

25215

S/062/61/000/007/005/009
B117/B215

The obtained compounds were identified by elementary analysis according to the content of hydroxyl groups, molecular weight, and ultrared spectra. It was shown that the reaction did not follow the scheme



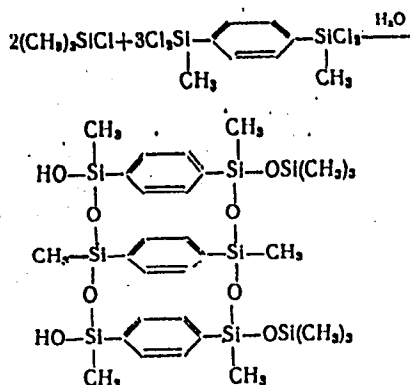
as expected, but that products with hydroxyl groups were always formed. Even under different reaction conditions (longer duration), the products always contained hydroxyl groups. Hence, the reaction follows schemes

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Reaction of cohydrolysis ...

25215

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B117/B215



(2)

This shows that cohydrolysis of the examined substances is difficult. Despite its considerable excess, trimethyl chlorosilane only reacts at a molar ratio of 1:1 or 1:1.5. This shows that the high rate of bis-(methyl-dichloro silyl)-benzene hydrolysis causes polycondensation of initial products of cohydrolysis. The cyclic compounds obtained

Card 5/6

26401
S/062/61/000/008/005/010
B117/B206

53700

AUTHORS: Andrianov, K. A., and Kuznetsova, I. K.

TITLE: The reactions of chloromethyl methylalkoxysilanes with sodium salts of diethyl phosphoric and dimethyl phosphinic acids

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 8, 1961, 1454-1456

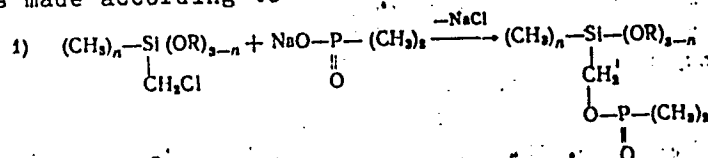
TEXT: The authors investigated the substitution of chlorine in α -chloro-methyl-alkoxy-silanes by dialkyl phosphoric- and phosphinic acid rests. The sodium salt of diethyl phosphate was prepared according to the method described in Ref. 3 (Canad. J. Chem. 34, 1819 (1956)) and carefully dried in a vacuum exsiccator over phosphorus pentoxide. The sodium salt of phosphinic acid was produced in the usual way by neutralization of dimethyl phosphinic acid in absolute alcohol, dried in a drying chamber for several hours at 120° to 130°C and stored in the vacuum exsiccator over P₂O₅. The experiments were made in a three-necked flask with mixer and

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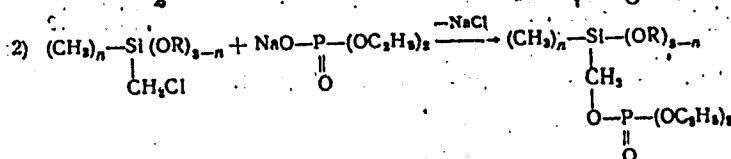
S/062/61/000/008/005/010
B117/B206

The reactions of chloromethyl...

sealing, rec cooler with calcium chloride tube and thermometer. The experiments showed that chlorine in α -chloromethyl alkoxysilanes easily reacts with the sodium salts mentioned. Organic compounds containing Si and P with an Si-C-O-P bond are formed thereby, containing simultaneously functional groups at the silicon atom. The synthesis of the compounds mentioned was made according to



and



where $\text{R}=\text{C}_2\text{H}_5$; $\text{Si}(\text{CH}_3)_2$, $n=1,2$. The yield of the products showed that the

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20411
S/062/61/000/008/005/010
B117/B206

The reactions of chloromethyl...

salt of dimethyl phosphinic acid reacts more easily. New organic compounds containing Si and P were obtained as results of the reactions carried out: methyldiethoxysilyl methylester of dimethyl phosphinic acid (I); dimethyl ethoxysilyl methylester of dimethyl phosphinic acid (II); methyldiethoxysilyl methylester of diethyl phosphinic acid (III); dimethyl ethoxysilyl methylester of diethyl phosphoric acid (IV); tetramethylsiloxy-1,2-disilyl methylester of dimethyl phosphinic acid (V). The properties of these compounds are comprised in the Table. There are 1 table and 3 non-Soviet references. The three references to English-language publications read as follows: A. Canavan, C. Eatorn, J. Chem. Soc. 1959, 3751; W. Garden, N. Thompson, Angl. pat. 815231; 24, 06, 1959; R. McIvor, C. McCarthy, C. Grant, Canad. J. Chem. 34, 1819 (1959).

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds, AS USSR)

SUBMITTED: October 12, 1960

Card 3/4

15-8170

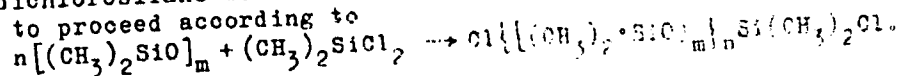
26402
S/062/61/000/008/006/010
B117/B206

AUTHORS: Andrianov, K. A., Severnyy, V. V., and Zavin, B. G.

TITLE: Telomerization reaction of dimethyl cyclosilanes.
Communication I. Production of linear α,ω -dichloro-
dimethyl siloxanes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 8, 1961, 1456-1461

TEXT: The authors investigated the telomerization of hexamethyl-cyclo-
trisiloxane and octamethyl-cyclotetrasiloxane with dimethyl-di-chloro-
silane, as well as the effect of the ratio of octamethyl-cyclotetra-
siloxane to dimethyl-dichlorosilane on the composition of the reaction
products. The following were used for the synthesis: crystalline
hexamethyl-cyclotrisiloxane, melting point 62-64°C, boiling point
132-136°C; octamethyl-cyclotetrasiloxane, boiling point 174-176°C;
dimethyl-dichlorosilane with a chlorine content of 55.7%. The reaction
was found to proceed according to

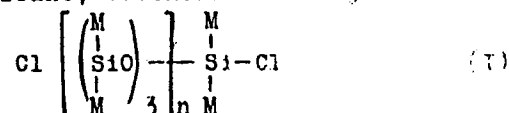


Card 1/6

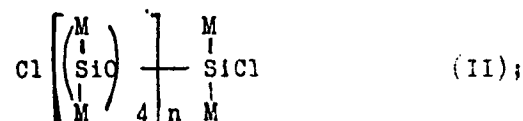
Telomerization reaction of dimethyl...

26402
S/062/61/000/008/006/010
R117/R206

From the reaction of equimolecular amounts of hexamethyl-cyclotrisiloxane and dimethyl-dichlorosilane, telomers of the joint formula



are formed in the dry stainless-steel autoclave at 250°C within 3 hr; from them, 38.5 % telomers with n=1, 24.1 % with n=2, 4.47 % with n=3 and 0.63 % with n=4. Under the same conditions, octamethyl-cyclotetra-siloxane with dimethyl-dichlorosilane yields products which follow the formula:



from them, 36.86 % with n=1, 32.95 % with n=2 and 7.47 % with n=3. The properties of the telomers which follow formulas (I) and (II) as well as analysis results are listed in Table 1. The investigation of the physical properties of the links of the homologous series of α,ω-dichloro-

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Telomerization reaction of dimethyl...

S/062/61/000/008/006/010
B117/B206

methyl siloxanes showed that conformable to law boiling points, specific gravities and refractive indices change with the number of silicon atoms in the molecule. No anomalies are observed in this connection. The telomerization of octamethyl-cyclotetrasiloxane with dimethyl-dichlorosilane was investigated at different molar ratios of the components: 1:1, 2:1 and 3:1. Experiments showed (Fig. 3) that telomerization does not yield pure products for any of the ratios investigated. Telomer mixtures with maximum yield of the product corresponding to the ratio concerned, develop continually. When increasing the ratio of the reacting components, the yield of low telomers is reduced and the amount of high-boiling products is greatly increased. There are 3 figures, 5 tables, and 2 references: 1 Soviet and 1 non-Soviet. The reference to the English-language publication reads as follows: W. Patnode, D. Wilcock, J. Amer. Chem. Soc. 68, 2291 (1946).

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds, AS USSR)

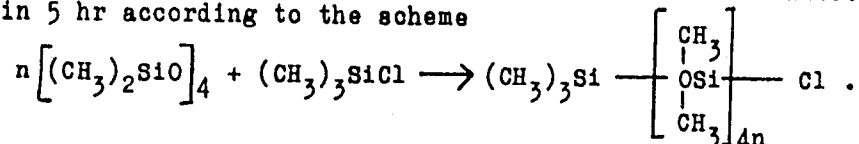
Card 3/6

27490

S/062/61/000/009/005/014
B117/B101

Telomerization of dimethyl ...

where m denotes the number of silicon atoms in the initial ring, $n = 1, 2, 3$ etc. In this study, the monofunctional trimethyl-chloro silane and not a difunctional compound was used as chain-terminating substance for the telomerization of dimethyl cyclosiloxanes. Equimolar amounts of octamethyl cyclotetrasiloxane and trimethyl-chloro silane telomerize in an autoclave at 250°C within 5 hr according to the scheme



Pure telomers with $n = 2, 3$, and 4 were obtained from the reaction mixture by fractional distillation. The physical constants of the telomers are listed in Table 1. The physical properties exhibit no anomalies. Tests carried out with various molar ratios of octamethyl cyclotetrasiloxane to trimethyl-chloro silane showed that at ratios of 1 : 1, 2 : 1, and 3 : 1 mixtures of telomers only, and no pure compounds were formed. In all of these mixtures the telomer formed in maximum quantity did not correspond to the stoichiometric ratio of the reactants. The telomer having a chain by 4 dimethyl-siloxane units longer than would correspond to the

Card 2/4

15.8170

27491
S/062/61/000/009/006/014
B117/B101

AUTHORS: Andrianov, K. A., Zhdanov, A. A., and Odinets, V. A.
TITLE: Synthesis of liquid 1,n-hexamethyl-poly(phenyl-ethyl)-methyl
siloxanes and investigation of their properties
PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 9, 1961, 1615-1624

TEXT: The lowest-molecular members of the polymerhomologous series of
1,n-hexamethyl-poly(phenyl-ethyl)-methyl siloxanes were synthesized and
their properties studied. The work was undertaken to study the dependence
of the polar properties of these liquid organo-silicon polymers on various
polar substituents at the benzene ring. The polar properties were
studied on the basis of the activation energy of viscous flow and the
temperature dependence of the viscosity. The flowing initial substances
were used for the synthesis: (phenyl-ethyl)-methyl-dichloro silane
($C_6H_5C_2H_4(CH_3)SiCl_2$, b.p. $90^{\circ}-92^{\circ}C$ (5 mm Hg)), (tolyl-ethyl)-methyl-di-
chloro silane ($CH_3C_6H_4C_2H_4(CH_3)SiCl_2$, b.p. $103^{\circ}-105^{\circ}C$ (2 mm Hg)), (chloro-
Card 1/6

27491

S/062/61/000/009/006/014

B117/B101

Synthesis of liquid 1,n-hexamethyl-

phenyl-ethyl)-methyl-dichloro silane ($\text{ClC}_6\text{H}_4\text{C}_2\text{H}_4(\text{CH}_3)\text{SiCl}_2$, b.p. $124^\circ\text{--}126^\circ\text{C}$ (2 mm Hg). The synthesis of these compounds is described in Ref. 11 (K. A. Andrianov, et al. Zh. obshch. Khimii (in print)). The liquid polymers were obtained by the joint hydrolysis of toluene solution of mixtures of these compounds with trimethyl-chloro silane (b.p. $58^\circ\text{--}59^\circ\text{C}$) at $90\text{--}95^\circ\text{C}$. Polymers of varying degrees of polymerization, according to the reactant ratio, may be isolated from the reaction mixture (Table 1). Hydrolysis of ethereal solution of (phenyl)-methyl-dichloro silane yielded cyclic polymers also: tri(phenyl-ethyl)-trimethyl cyclotrisiloxane $[\text{C}_6\text{H}_5\text{C}_2\text{H}_4(\text{CH}_3)\text{SiO}]_3$ and tetra(phenyl-ethyl)-tetramethyl cyclotetrasiloxane $[\text{C}_6\text{H}_5\text{C}_2\text{H}_4(\text{CH}_3)\text{SiO}]_4$. Evaluation of the infrared spectra of the compounds investigated indicates that the addition of the vinyl aromatic nucleus takes place in β position, giving β -substituted derivatives. The density of the liquids was determined pycnometrically. Viscosity measurements were carried out by standard methods with an Ostwald-Pinkevich viscosimeter. Data on the activation energy of viscous flow and the temperature coefficients of the viscosity are shown in Table 2. It was found that for the lowest-molecular members of the homologous series the

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Synthesis of liquid 1,n-hexamethyl- ...

27491

S/062/61/000/009/006/014

B117/B101

activation energy of viscous flow is hardly dependent on the polar groups. Substitution of the hydrogen atom at the nucleus by methyl or chlorine, however, always increases the activation energy. The activation energy of flow depends on the number of silicon atoms in the polymers under study. The polar properties of the radicals investigated decreases in the order $-C_2H_4C_6H_4Cl > -C_2H_4C_6H_4CH_3 > -C_2H_4C_6H_5$. There are 12 figures, 2 tables, and 12 references: 7 Soviet and 5 non-Soviet. The three references to English-language publications read as follows: C. C. Currie, Industr. and Engng. Chem. 46, 2331 (1954); L. H. Sommer, R. P. Pioch, J. Amer. Chem. Soc. 75, 6337 (1953); L. H. Sommer, W. D. English, G. R. Ansul, D. N. Vivona, J. Amer. Chem. Soc. 77, 2485 (1955).

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

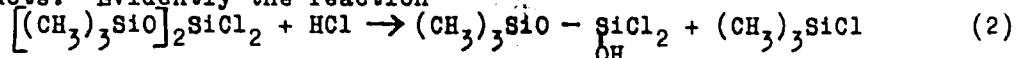
SUBMITTED: December 12, 1960

Card 3/6

27492
S/062/61/000/009/007/014
B117/B101

Reactions of bis(trimethyl- ...

products. Evidently the reaction



takes place. The trimethyl-chloro silane formed thereby is then transformed to a trimethyl-alkoxy silane by the excess alcohol present. This reaction, which was previously observed with trimethyl-siloxy groups bound to titanium (Ref. 1: K. A. Andrianov, N. A. Kurasheva, Dokl. AN SSSR 135, 316 (1960)) thus also occurs in the case of trimethyl-alkoxy groups bound to silicon. The presence of traces of moisture is of great importance for reaction (2). This is formed in the reaction $ROH + HCl \rightleftharpoons RCl + H_2O$. Since phenols do not react in this manner, the reaction of bis(trimethyl-siloxy)-dichloro silane with phenol leads to bis-(trimethyl-siloxy)-diphenoxy silane. The yield is 60.5%. To suppress the side-reaction caused by hydrogen chloride, methods were used in the experiments which either neutralize the hydrogen chloride or exclude its formation. Bis-(trimethyl-siloxy)-diethoxy silane was obtained in 68% yield by etherification of bis(trimethyl-siloxy)-dichloro silane with anhydrous ethyl alcohol in the presence of pyridine. Various bis(trimethyl-siloxy)-dialkoxy silane derivatives were prepared by treating

Card 2/4

Reactions of bis(trimethyl- ...

27492
S/062/61/000/009/007/014
B117/B101

in air and is easily soluble in toluene. There are 2 tables and 3 references: 2 Soviet and 1 non-Soviet. The reference to the English-language publication reads as follows: R. O. Sauer, J. Amer. Chem. Soc. 66, 1707 (1944).

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: February 2, 1961

Legend to Table 1.

- (1) Formula,
- (2) b.p., °C,
- (3) calculated,
- (4) found.

(1) Формула	(2) Т. кип., °C	n_D^{20}	d_4^{20}	MR	
				вычл. л-но	найдено
$[(CH_3)_3SiO]_2Si(OC_4H_9)_2$	232—234	1,4003	0,8847	90,94	90,81
$[(CH_3)_3SiO]_2Si(OC_4H_9)_2$	225—227	1,3968	0,8757	96,94	96,88
$[CH_3)_2SiO]_2Si(OC_4H_9)_2$	214—126	1,3943	0,8903	87,08	87,25
$[(CH_3)_2SiO]_2Si(OC_4H_9)_2$	202—203	1,3875	0,8752	87,68	87,31
$[(CH_3)_2SiO]_2Si(OC_2H_5)_2$	191—193	1,3870	0,8921	78,46	78,10
$[(CH_3)_2SiO]_2Si(OCH_3)_2$	174—175	1,3855	0,9155	60,16	68,84
$[(CH_3)_2SiO]_2Si(OC_4H_9)_2$	157—159 (3 мм)	1,4750	1,0330	100,50	100,85

Card 4/4

28271 S/062/61/000/010/006/018
B117/B101

5.3700

AUTHORS: Andrianov, K. A., and Severnyy, V. V.

TITLE: Telomerization of dimethyl cyclosiloxanes. Communication 3.
Telomerization by methyl vinyl dichloro silane and methyl
phenyl dichloro silane

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 10, 1961, 1788 - 1791

TEXT: Telomerization of octamethyl cyclotetrasiloxane by methyl vinyl
dichloro silane and methyl phenyl dichloro silane is described. The aim
of this paper was to investigate the effect of various substituents on
the course of reaction. In the experiments, octamethyl cyclotetrasiloxane
with boiling point 174° - 176°C, methyl vinyl dichloro silane with boiling
point 93°C (Cl 50.6%), and methyl phenyl dichloro silane with boiling
point 200° - 202°C (Cl 37.0%) were used. From the reaction of equi-
molecular quantities of octamethyl cyclotetrasiloxane and methyl vinyl
dichloro silane, a mixture of telomer homologs was formed. From this
mixture, α -chloro methyl vinyl siloxy- ω -chloro dimethyl siloxanes with

Card 1/4

Telomerization of dimethyl...

20271 S/062/61/000/010/006/018
B117/B101

n = 1, 2, and 3 were isolated and identified on the basis of boiling temperature, refractive indices, specific gravities, molecular refractions, results of elementary analysis, and bromine numbers. The properties of the compounds obtained are listed in Table 1. The mean conversion of vinyl methyl dichloro silane was 32.8%, and that of octamethyl cyclotetrasiloxane 54.0%. The yield of telomers was 45.1% by weight of the initial mixture. Contents of the individual telomer homologs with n = 1, 2, and 3 were 18.5, 30.8, and 14.6%, respectively. Higher telomers with a polymerization degree $n \geq 3$ were formed in the amount of 36.1%. Thus, it was established that telomerization is the only reaction at the moment by which compounds of the α -chloro methyl vinyl siloxy- ω -chloro dimethyl siloxane series with given atomic number may be obtained. The reaction of octamethyl cyclotetrasiloxane with methyl phenyl dichloro silane showed low conversion under standard conditions (3 hr, 250°C). Also the experiments with 2 M methyl phenyl dichloro silane and 1 M octamethyl cyclotetrasiloxane resulted in a total conversion of only 18.4% at 300°C in 5 hr. The conversion of methyl phenyl dichloro silane was 9.1%, and that of octamethyl cyclotetrasiloxane 19.0%. From the reaction products, telomer homologs with n = 1 and 2 were isolated. 49.0% of the telomers

Card 2/4

Telomerization of dimethyl...

20.2/1 S/062/61/000/010/006/018
B117/B101

had a boiling point higher than 350°C (3 mm). The properties of the resultant α -chloro phenyl- ω -chloro nonamethyl pentasiloxane and α -chloro phenyl- ω -8chloro heptadecamethyl nonasiloxane are listed in Table 2. Thus, it was proved that telomer homologs of the α -chloro methyl phenyl siloxy- ω -chloro dimethyl siloxane series are formed by the reaction of octamethyl cyclotetrasiloxane with methyl phenyl dichloro silane. There are 4 tables and 3 Soviet references.

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: March 23, 1961

Legend to Tables 1 and 2: (1) Formula; (2) boiling point, °C (p mmHg); (3) calculated; (4) found.

X

Card 3/4

53700

28272 S/062/61/000/010/007/018
B117/B101

AUTHORS: Andrianov, K. A., and Kuznetsova, I. K.

TITLE: Reaction of trialkyl(aryl)hydroxy silanes with methyl
ethoxy silyl methyl esters of dimethyl phosphinic acid

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 10, 1961, 1792 - 1794

TEXT: The authors investigated the substitution of the alkoxy group by dimethyl phosphinic acid radicals as the end groups on various organo-silicon compounds. It was found that by heating dimethyl ethoxy silyl methyl ester of dimethyl phosphinic acid with triethyl hydroxy silane at a ratio of 1:1, ethyl alcohol was separated at 140° - 150°C and 1-triethyl-3-dimethyl disiloxane methyl ester of dimethyl phosphinic acid was formed in 60% yield. From the reaction of dimethyl ethoxy silyl methyl ester of dimethyl phosphinic acid with dimethyl phenyl hydroxy silane or with methyl diphenyl hydroxy silane, 1-dimethyl phenyl-3-dimethyl disiloxane methyl ester of dimethyl phosphinic acid and 1-methyl diphenyl-3-dimethyl disiloxane methyl ester of dimethyl phosphinic acid, respectively, were obtained.

Card 1/4

Reaction of trialkyl...

28272 S/062/61/000/010/007/018
B117/B101

Not only one but two ethoxy groups are substituted on the silicon atom. Thus, from the reaction of dimethyl phenyl hydroxy silane with methyl diethoxy silyl methyl ester of dimethyl phosphinic acid at a ratio of 2:1, 1,5-dimethyl phenyl-3-methyl trisiloxane methyl ester of dimethyl phosphinic acid was obtained. Similar reactions were conducted with triethyl- and dimethyl diphenyl hydroxy silanes. All reactions were conducted without a catalyst. The dimethyl phenyl hydroxy silane and methyl diphenyl hydroxy silane used were produced by the method of K. A. Andrianov and N. Delazari (Ref. 3: Dokl. AN SSSR 122, 3, 393 (1958)), and dimethyl ethoxy silyl methyl ester and methyl diethoxy silyl methyl ester of dimethyl phosphinic acid by the authors' method described in Ref. 4 (Izv. AN SSSR, Otd. khim. n. 1961, 1454). Ethyl alcohol produced during the reaction was distilled off and identified on the basis of boiling temperature and refractive index. Reactions conducted yielded compounds not yet described with 2 or 3 silicon atoms containing a dimethyl phosphinic group. The compounds obtained are colorless liquids readily soluble in organic solvents and may be distilled in vacuum. Their properties are listed in the table. There are 1 table and 4 references; 2 Soviet and 2 non-Soviet.

Card 2/4

Reaction of trialkyl...

25272 S/062/61/000/010/007/018
B117/B101

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk
SSSR (Institute of Elemental Organic Compounds of the
Academy of Sciences USSR)

SUBMITTED: April 6, 1961

Legend to the Table: (1) number; (2) structural formula; (3) boiling
point, °C (p mm Hg); (4) found; (5) calculated.

Card 3/4

15.8140

28987

S/191/61/000/011/003/008

B110/B147

11.2212

AUTHORS: Andrianov, K. A., Pakhomov, V. I., Lapteva, N. Ye.

TITLE: Reactions of hydroxy-methyl-methyl siloxanes with acids and isocyanates

PERIODICAL: Plasticheskiye massy, no. 11, 1961, 17-20

TEXT: The stability of the hydroxyl group being in α -position to the Si atom, and its reaction with acids and isocyanates is investigated on the example of bis-(hydroxy-methyl)-tetramethyl disiloxane (A) and poly-(hydroxy-methyl-methyl)-siloxane (B). For the preparation of A

according to $\text{CH}_3\text{COOCH}_2(\text{CH}_3)_2\text{Si-O-Si}(\text{CH}_3)_2\text{CH}_2\text{OOCCH}_3 + 2\text{CH}_3\text{OH}$

$\xrightarrow{\text{HCl}}$ $\text{HOCH}_2(\text{CH}_3)_2\text{Si-O-Si}(\text{CH}_3)_2\text{CH}_2\text{OH} + 2\text{CH}_3\text{COOCH}_3$, 60 g of bis-(acetoxy-methyl)-tetramethyl disiloxane were methanolized by means of 240 ml CH_3OH with 1-1.2 % HCl. 5 g of anion exchanger AH-2 Φ (AN-2F) or AH-18

(AN-18) in the OH form lower the HCl content to 0.05-0.02 %. The yield of

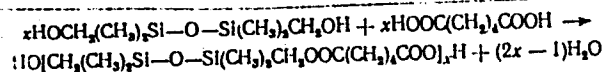
Card 1/05

28987 S/191/61/000/011/003/008
B110/B147

Reactions of hydroxy-methyl-methyl...

unpurified A is 91 % of the theoretical amount (45.7 g): $n_D^{20} = 1.4355$;
 $d_4^{25} = 0.7989$; OH content = 16.47 %; Si content = 29.86 %; MW = 210.

Rectification at $5 \cdot 10^{-1}$ mm Hg produced crystalline, pure A (melting point $\sim 8^\circ\text{C}$). (Table 1). Experiments proved a comparatively difficult condensation of the hydroxyl groups of A (Table 2). Only when small amounts of acid are introduced into A, its properties change slowly. Heating of A for 15 hr at 200°C lowers the OH content from 16.95 to 14.36 %. Esterification of 6.98 g of A by means of 5.26 g of adipic acid (molar ratio 1:1) proceeded readily at 200°C :



The ester number increases quickly during polycondensation, the acid number drops after 15 hr of heating. The polymer with acid number 8.3, ester number 338, and MW 9500 was a viscous, highly sticky brown liquid, soluble in alcohols, ethers, hydrocarbons, ketones, dioxane, tetrahydrofuran, acetic acid, and formic acid. The polyester was treated at 200°C

Card 2/7

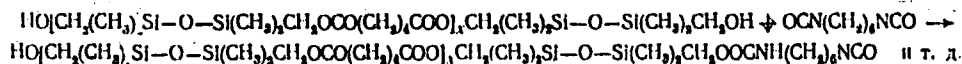
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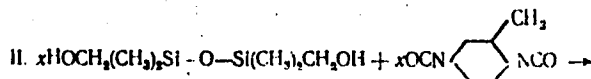
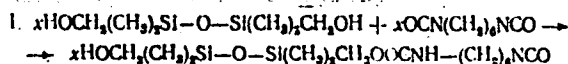
B110/B147

Reactions of hydroxy-methyl-methyl...

and 10 mm Hg with 0.37 g of A for esterification of the terminal COOH groups. 2.023 g of polyester with 0.0516 g of hexamethylene diisocyanate (C) (0.5 g-mole to 1 COOH group) at 200°C in 10 % acetic acid solution in the N₂ flow produced an elastic, rubber-like polymer:



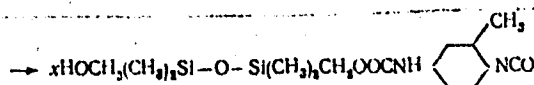
This dissolves in acetic acid and formic acid, and swells in tetrahydrofuran, dioxane, hydrocarbons, and pyridine. 3.06 g of A at 120°C with 2.7 g of C form sticky, elastic polymers well adhering to glass and duralumin in 1.5 % alcoholic solution. 3.4 g of A at 120°C with 2.9 g of p-toluylene diisocyanate form solid polymers in 1 % acetic acid solution



Card 3/7

Reactions of hydroxy-methyl-methyl...

28987 S/191/61/000/011/003/008
B110/B147



I dissolves in aliphatic alcohols and cresol, I and II in acetic acid and formic acid. They swell in pyridine, hydrocarbons, and tetrahydrofuran. 15 g of A were mixed with 50 g of 2 % HCl, stirred at 90°C for 15 hr, and the content of acetic acid was determined. It was neutralized by means of solid NaHCO₃ and determined in %: Si = 20.5; OH = 3.41; CH₃COO = 24.18.

20 g of A was stored for 48 hr at 20°C, and viscosity as well as refractive index were determined (Table 2). After heating 5 g of A at 200°C for 15 hr, the OH content drops from 16.95 to 14.36 %. During the effect of 0.4 g of 98 % H₂SO₄ on 15 g of A, η_{20} and n_D^{20} remained nearly unchanged even after a longer effect. When 10.72 g of A was left standing for 48 hr with 40.98 CH₃OH acidified with 35 % HCl, the Si and OH content remained practically constant. The same applied when 4.97 g of A was left standing for 48 hr with 0.64 g of distilled water. There are 4 figures, 4 tables, and 3 references: 1 Soviet and 2 non-Soviet.

Card 4/7

Reactions of hydroxy-methyl-methyl...

28987
S/191/61/000/011/003/008
B110/B147

The two references to English-language publications read as follows:
Speier, J. Am. Chem. Soc., 74, 1474 (1949); Us Pat. 2527590 (1950);
C. A., 45, 2498 (1951).

Table 1. Effect of 2 % HCl and H₂SO₄ on bis-(acetoxymethyl)-tetramethyl disiloxane.

Legend: (1) Amount of bis-(acetoxymethyl)-tetramethyl disiloxane, g;
(2) acid used; (3) experimental conditions; (4) content, %; (5) molecular weight; (6) acetoxy group cleavage, %; (7) initial bis-(acetoxymethyl)-tetramethyl disiloxane; (8) designation; (9) amount, ml; (10) time, hr; (11) temperature, °C; (12) OH groups; (13) 2 % H₂SO₄; (14) 2 % HCl.

Table 2. Effect of heating on bis-(hydroxy-methyl)-tetramethyl disiloxane.

Legend: (1) Temperature, °C; (2) time, min; (3) viscosity, $\eta_{20} \text{ cm}^3$.

Card 5/7

Reactions of hydroxy-methyl-methyl...

S/191/61/000/011/003/008
R110/B147

For Tables see Cards 7/8 and 8/8.

Card 6/8

5.3700

29519
S/062/61/000/011/006/012
B103/B147

AUTHORS: Andrianov, K. A. and Volkova, L. M.

TITLE: Reaction of aryl-(alkyl-)amino-methyl-ethoxy silanes with
alkyl-(aryl-)hydroxy silanes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 11, 1961, 2003 - 2006

TEXT: The paper deals with the reaction of aryl-(alkyl-)amino-methyl-ethoxy
silanes $XCH_2CH_2Si(OC_2H_5)_2$ with (a) triethyl-hydroxy silane, (b) dimethyl-
phenyl-hydroxy silane, and (c) diethyl-dihydroxy silane, X being C_6H_5NH- ,

$(C_2H_5)_2N-$, ClC_6H_4NH- , $O \begin{array}{c} CH_2CH_2 \\ CH_2CH_2 \end{array} N-$. It has been found that the introduction

of one amino group into the organic radical in alpha position to the Si
atom increases the exchangeability of the alkoxy group for the triethyl-
or dimethyl-phenyl-siloxy groups. The reaction takes place readily and
without catalysts as follows: $XCH_2CH_2Si(OC_2H_5)_2 + 2(C_2H_5)_3SiOH \rightarrow$

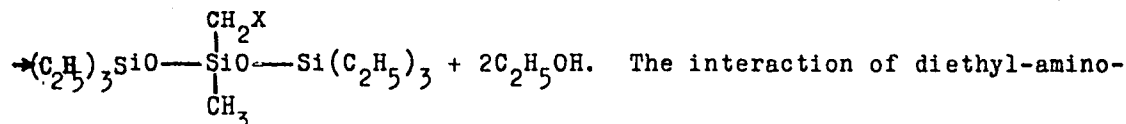
Card 1/4

Reaction of aryl-(alkyl-)amino-...

29519

S/062/61/000/011/006/012

B103/B147



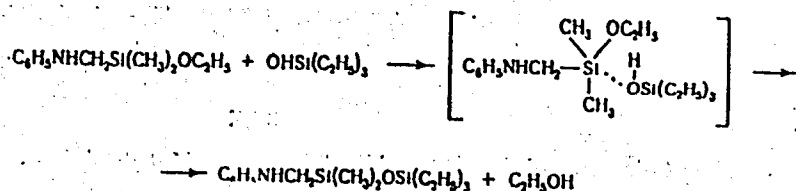
The interaction of diethyl-amino-methyl-(methyl-)diethoxy silane and (a) at room temperature results in the heating of the mixture. If the reaction mixture is heated gradually up to 150°C, more than 70% of alcohol is distilled off. 1, 1, 1, 3, 3, 3-hexaethyl-2-methyl-2-diethyl-amino-methyl trisiloxane was separated by fractionation of the reaction products (yield 78.5%). Phenyl-amino-methyl-dimethyl-ethoxy silane reacts with b) equally well. Already within the first hour of heating more than 70% of alcohol was separated and 1, 1, 2, 2-tetramethyl-1-phenyl-amino-methyl-2-phenyl disiloxane was formed. In the above cases, one alkoxy group is substituted by the triethyl- or dimethyl-phenyl-siloxy groups just as readily as two. The reaction of c) with phenyl-amino-methyl-dimethyl-ethoxy silane is much more complicated. Two products were separated: 1, 1, 3, 3-tetramethyl-2,2-diethyl-1,3-di(phenyl-amino-methyl) trisiloxane and bis-(phenyl-amino-methyl)-tetramethyl disiloxane. The reaction does not only take place as follows:

Card 2/64

Reaction of aryl-(alkyl-)amino...

29519
S/062/61/000/011/006/012
B103/B147

hydroxy silanes according to the following mechanism:



There are 1 table and 3 non-Soviet references. The reference to the English-language publication reads as follows: L. J. Tyler, US-Patent 2611774; 23. IX. 1952; Chem. Abstr. 47, 4129 (1953).

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

Card 4/4

53700

30164
S/062/61/000/012/003/012
B118/B147

AUTHORS: Andrianov, K. A., and Delazari, N. V.

TITLE: Reactions of trimethyl siloxychloro silanes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 12, 1961, 2169 - 2173

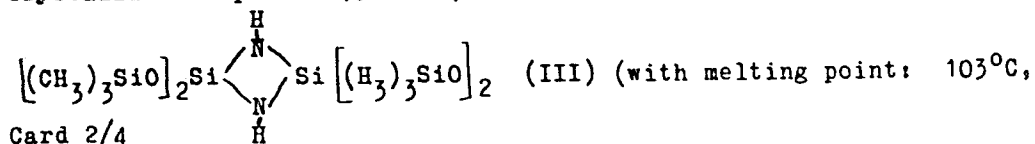
TEXT: Since reactions of trimethyl siloxychloro silanes with nucleophilic and electrophilic compounds so far have not been sufficiently studied, the authors showed in a previous paper the high reactivity of the trimethyl siloxy group in bis-(trimethyl siloxy)-dichloro silane where the Si-O-Si bond is unexpectedly ruptured. In the present work, other reactions of compounds containing a trimethyl siloxy group on the silicon atom have been studied. It was shown that tris-(trimethyl siloxy)-hydroxy silane did not react with tetrabutoxy titanium and tin tetrachloride on heating for a longer period in the presence of NH_3 . When heated in the presence of HCl , tris-(trimethyl siloxy)-hydroxy silane does not form a dimer, and the initial product remains unchanged. Reac-

Card 1/4

Reactions of trimethyl...

3016B
S/062/61/000/012/003/012
B118/B147

tion between NH_3 and bis-(trimethyl siloxy)-dichloro silane in benzene at room temperature yielded two products: bis-(trimethyl siloxy)-diamino-silane and 1,3-bis-(trimethyl siloxy)-1,3-aminodisilosane according to the formulas $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{NH}_2)_2$ (I) (53.1%) (boiling point $51 - 53^\circ\text{C}$ (3 mm Hg); $n_D^{20} = 1.4057$; $d_4^{20} = 0.9066$; MR (determined) 64.43) and $[(\text{CH}_3)_3\text{SiO}]_2 - \underset{\text{NH}_2}{\text{Si}} - \text{NH} - \underset{\text{NH}_2}{\text{Si}} - [(\text{CH}_3)_3\text{SiO}]_2$ (II) (22.2%) (boiling point: $117 - 119^\circ\text{C}$ (3 mm Hg); $n_D^{20} = 1.4119$; $d_4^{20} = 0.9338$; MR = 122.28). Unlike hydrolysis, aminolysis yielded no complex, insoluble polymers. Hence, the trimethyl siloxy group was not separated. Heating compound (I) at $212 - 304^\circ\text{C}$ for a longer period and with liberation of NH_3 yielded the crystalline compound 1,3-bis-(trimethyl siloxy)-cyclosilosane:



Reactions of trimethyl...

30161
S/062/61/000/012/003/012
B118/B147

boiling point: 180 - 183°C (4 mm Hg)). To confirm its structure, compound (III) was also obtained from 1,3-bis-(trimethyl siloxy)-1,3-amino-disilosane by 25 hr heating at 280 - 344°C. Separation of the trimethyl siloxy group and formation of insoluble products were not observed on aminolysis. Above 150°C, tris-(trimethyl siloxy)-hydroxy silane reacts with Na with formation of H_2 , tetrakis-(trimethyl siloxy)-silane, $[(CH_3)_3SiO]_4Si$ (5.3%), and tris-(trimethyl siloxy)-sodium oxy-silane (17.9%). In the formation of the former, the Si-O-Si bond is ruptured. On heating tris-(trimethyl siloxy)-hydroxy silane and $TiCl_4$ for a longer period, no reaction occurs, whereas reaction between $TiCl_4$ and $[(CH_3)_3SiO]_3SiONa$ yields tetrakis- $[(CH_3)_3SiO]_4Si$ titanium: $\{[(CH_3)_3SiO]_3SiO\}_4Ti$ where the Si-O-Si bond is not ruptured (boiling point: 223 - 225°C (1.5 mm Hg); $n_D^{20} = 1.4201$; $d_4^{20} = 0.9623$; MR = 341.9). X

Irrespective of the high molecular weight and the 80.7% inorganic portion, this compound is an easily mobile liquid. These properties are explained by the cross-type structure $-Ti-$ where the inorganic portion of the

Card 3/4

5.3700

25040
S/062/61/001/006/002/010
B118/B220

AUTHOR: Andrianov, K. A., Vasil'yeva, T. V.,
and Khananashvili, L. M.

TITLE: Condensation of methyl phosphinic acid
with α, ω - diethoxy-dimethyl siloxanes

PERIODICAL: Akademiya nauk SSSR. Izvestiya.
Otdeleniye khimicheskikh nauk, v. 1, no. 6, 1961, 1030-1035

TEXT: The present paper deals with the condensation of α, ω -diethoxy-dimethyl siloxanes with methyl phosphinic acid. This reaction proved to be an easy method of synthesizing the mixed organo-silicon phosphorus compounds resulting primarily in the formation of cyclic, not high-polymer compounds. An increase of the distance between the alkoxy groups in α, ω -diethoxy-dimethyl siloxanes does not alter the direction of the reaction. In any case, the reaction proceeds according to the following equation

Card 1/4

25040

S/062/61/001/006/002/010

B118/B220

Condensation of methyl phosphinic...

cyclodi (methyl phosphinoxy) disiloxane. On condensation of methyl phosphinic acid with α, ω -diethoxy-dimethyl siloxane, the siloxane bond splits to form hexamethyl cyclomethyl phosphinoxy trisiloxane if $n = 5$, whereby only a small amount of decamethyl cyclomethyl phosphinoxy-pentasiloxane is separated. The resulting colorless, viscous liquids distillable in vacuo are hydrolyzed already by atmospheric moisture. Infrared absorption spectra (besides the analytical data) were studied to establish the composition and structure of hexamethyl cyclomethyl phosphinoxy-trisiloxane, tetramethyl phosphinoxy-disiloxane, and tetramethyl cyclodi (methyl phosphinoxy)disiloxane. The bands characteristic of the groups: CH_3 ; Si-CH_3 ; $\text{P} = \text{O}$; and Si-O-Si were detected in these spectra. The spectra of hexamethyl cyclomethyl phosphinoxy-trisiloxane, tetramethyl cyclodi(methyl phosphinoxy)disiloxane, tetramethyl cyclomethyl phosphinoxy-disiloxane show absorption bands of the groups Si-O-P and Si-O-Si . In order to confirm the structure of hexamethyl cyclomethyl phosphinoxy-trisiloxane, tetramethyl cyclomethyl phosphinoxydisiloxane, and tetramethyl di(methyl phosphinoxy)disiloxane, these compounds were submitted to a hydrolytic decomposition. The water destroys the latter according to

Card 3/4

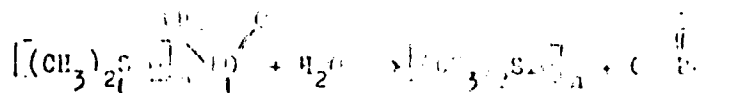
25040

S/062/61/001/006/002/010

E118/E22

Condensation of methyl phosphonic...

the following equation.



This hydrolysis results in by-product also. A. P. Gith... is thanked for taking the infrared spectra of the compounds obtained. There are 3 figures, 3 tables, and 1 non-Soviet-bloc reference. The reference to English-language publication reads as follows: P. Hoyer, J. Amer. Chem. Soc. 71, 2918 (1949).

ASSOCIATION: Institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Institute of Fine Chemical Technology im. M. V. Lomonosov)

SUBMITTED: July 6, 1960

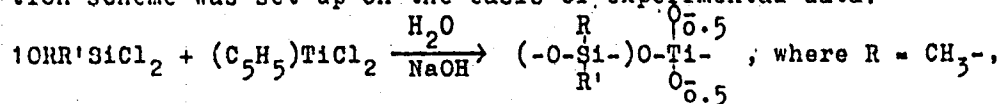
Card 4/4

21133

S/190/61/003/004/008/014
B101/B207

Reactions of ...

but was accompanied by a splitting off of cyclopentadienyl groups (CPD) owing to the readily hydrolyzable C-Ti bond. Chemical analysis of the polymer yielded an initial ratio Ti : Si atoms = 1 : 10, the C content, however, indicated that CPD groups had been split off. To study hydrolysis more closely, dimethyl dichloro silane was cohydrolyzed in acid medium with bis-(cyclopentadienyl)-dichloro titanium in acid medium without acceptor. Thus, the CPD groups were completely split off and octamethyl cyclotetrasiloxane and TiO_2 formed. Cohydrolysis of the titanium compound with diethyl dichloro silane and methyl-phenyl dichloro silane led to the same results as with dimethyl dichloro silane. These polymers were viscous liquids. The infrared spectra showed the 920 cm^{-1} band of the Ti-O-Si group. The following reaction scheme was set up on the basis of experimental data:



$R' = CH_3-$ (I); $R = C_2H_5$, $R' = C_2H_5-$ (II); $R = CH_3-$, $R' = C_6H_5$ (III). To avoid hydrolysis, B), the exchange reaction between the di-sodium salts of

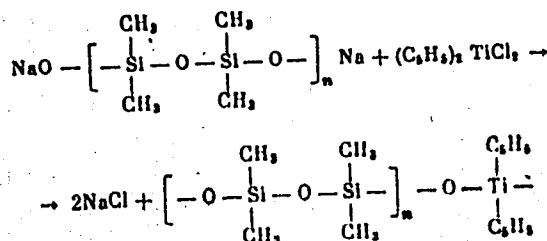
Card 2/5

21133

S/190/61/003/004/006/014
B101/B207

Reactions of ...

1,3-dihydroxy tetramethyl siloxane or 1,5-dihydroxy octamethyl tetrasiloxane was carried out with bis-(cyclopentadienyl)-titanium in benzene solution at 80°C. Yellow polymers which are soluble in toluene or xylene were obtained in a 77-80% yield. The atomic ratio Si : Ti was 2 : 1 or 4 : 1. Apart from the exchange reaction:



however, also CPD groups were split off. Infrared spectra revealed the absence of the 770 cm⁻¹ band which corresponds to one CPD group on Ti, and the presence of the 870 cm⁻¹ band which corresponds to two CPD groups on the Ti atom, as well as the bands 1020 and 1050 cm⁻¹ of the Si-O group in six-membered or multi-membered cycles. Herefrom, the following structural

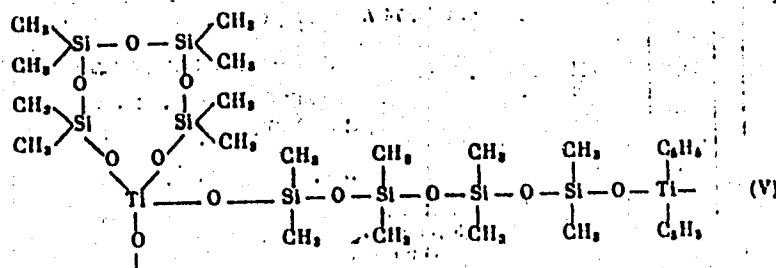
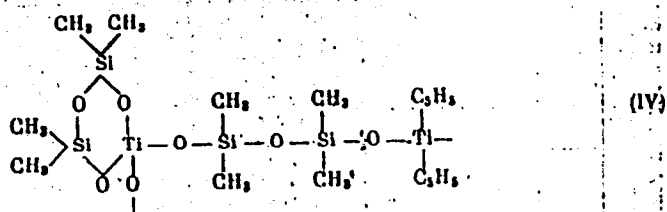
Card 3/5

21133

S/190/61/003/004/008/014
B101/B207

Reactions of ...

formula was derived for the links of the polymer chain:



Card 4/5

21133

Reactions of ...

S/190/61/003/004/008/014
B101/B207

The vitrification temperature of polymer IV was approximately 12°C, while that of V was below 0°C. IV showed no flow when heated up to 250°C, while with flow occurred when heated to 100°C. Both polymers became insoluble after having been heated to 200°C. Thus, it may be concluded that structuration occurred. After evaporation of the solvent, the soluble polymers formed films. The authors thank the collaborators of the opticheskaya laboratoriya (Optics Laboratory), headed by I. V. Obreimov, and those of the laboratoriya issledovaniya polimerov (Laboratory for Polymer Studies), headed by G. L. Slonimskiy, for their ready cooperation. There are 2 figures, 1 table, and 3 references: 1 Soviet-bloc and 2 non-Soviet-bloc. The 2 references to English-language publications read as follows: C. L. Sloan, W. A. Barber, J. Amer. Chem. Soc., 81, 1364, 1959; G. Wilkinson, I. M. Birmingham, J. Amer. Chem. Soc., 76, 4281, 1954.

ASSOCIATION: Institut elementoorganicheskikh soedineniy AN SSSR
(Institute of Elemental Organic Compounds, AS USSR)

SUBMITTED: July 13, 1960

Card 5/5

15-8170

11.2212

25259

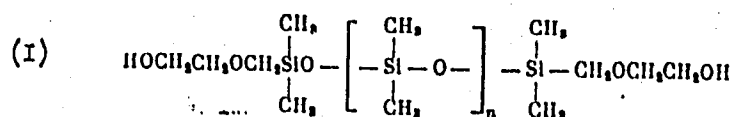
S/190/61/003/007/003/021
B101/B208

AUTHORS: Andrianov, K.A., Makarova, L.I.

TITLE: Reaction of bivalent organosilicon alcohols with diisocyanates

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 7, 1961
966-970

TEXT: The authors report on the reaction of bivalent alcohols of the polydimethyl siloxane series with the general constitutional formula:



with m-toluylene and with hexamethylene-diisocyanate. The alcohols were synthesized 1) by interaction of bis- (chloro methyl)-tetramethyl

Card 1/4

Reaction of bivalent ...

25259

S/190/61/003/007/003/021
B101/B208

disiloxane with sodium glycolate. The alcohol was here obtained with $n = 0$. 2) By cohydrolysis of dimethyl diethoxy silane with heterocyclic

dimethyl alkoxy silane $(CH_3)_2Si \begin{matrix} O-CH_2 \\ | \\ CH_2-O \end{matrix} CH_2$. In this case, the alcohols

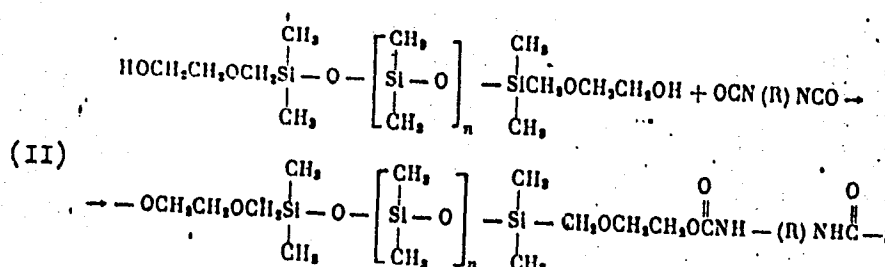
were obtained with $n = 10, 12, 14$ and 20 . The reaction with the diisocyanates was carried out at $190^\circ C$ without solvent. The intrinsic viscosity of the end product was found to depend on the alcohol applied. It decreased with increasing n (increasing distance between the OH groups). The condensation product with hexamethylene diisocyanate had an intrinsic viscosity of 0.45 at $n = 0$, and of 0.11 at $n = 20$. Polymer analysis indicated that the reaction proceeds according to the formula

Card 2/4

Reaction of bivalent ...

25259

S/190/61/003/007/003/021
B101/B208



Neither a separation of siloxane- nor of Si-C bonds occurs. The resultant polymers were elastic and rubberlike at room temperature. They were only soluble in cresol, but not in other organic solvents. The study of the thermomechanical properties disclosed: 1) The condensation product with toluylene diisocyanate had a vitrification temperature of +20°C, if alcohol with n = 0 was used. At n = 20, the vitrification temperature was -95°C. 2) In the case of hexamethylene diisocyanate, the vitrification temperature

Card 3/4